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## **Radiation Chemistry of Salt-Mine Brines and Hydrates**

G. H. Jenks  
J. R. Walton |

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RADIATION CHEMISTRY OF SALT-MINE BRINES AND HYDRATES

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RADIATION CHEMISTRY OF SALT-MINE BRINES AND HYDRATES

G. H. Jenks  
J. R. Walton\*

## ABSTRACT

Certain aspects of the radiation chemistry of NaCl-saturated  $\text{MgCl}_2$  solutions and  $\text{MgCl}_2$  hydrates at temperatures in the range of 30 to 180°C were investigated through experiments. A principal objective was to establish the values for the yields of  $\text{H}_2$  [ $G(\text{H}_2)$ ] and accompanying oxidants in the gamma-ray radiolysis of concentrated brines that might occur in waste repositories in salt.

We concluded that  $G(\text{H}_2)$  from gamma-irradiated brine solution into a simultaneously irradiated, deaerated atmosphere above the solution is between 0.48 and 0.49 over most of the range 30 to 143°C. The yield is probably somewhat lower at the lower end of this range, averaging 0.44 at 30 to 45°C. Changes in the relative amounts of  $\text{MgCl}_2$  and NaCl in the NaCl-saturated solutions have negligible effects on the yield.

The yield of  $\text{O}_2$  into the same atmosphere averages 0.13, independent of the temperature and brine composition, showing that only ~50% of the radiolytic oxidant that was formed along with the  $\text{H}_2$  was present as  $\text{O}_2$ . We did not identify the species that compose the remainder of the oxidant.

We concluded that the yield of  $\text{H}_2$  from a gamma-irradiated brine solution into a simultaneously irradiated atmosphere containing 5 to 8% air in He may be greater than the yield in deaerated systems by amounts ranging from 0% for temperatures of 73 to 85°C, to about 30 and 40% for temperatures in the ranges 100 to 143°C and 30 to 45°C, respectively. We did not establish the mechanism whereby the air affected the yields of  $\text{H}_2$  and  $\text{O}_2$ .

The values found in this work for  $G(\text{H}_2)$  in deaerated systems are in approximate agreement with the value of 0.44 for the gamma-irradiation yield of  $\text{H}_2$  in pure  $\text{H}_2\text{O}$  at room temperature. They are also in agreement with the values predicted by extrapolation from the findings of previous researchers for the value for  $G(\text{H}_2)$  in 2 M NaCl solutions at room temperature. They are in poorer agreement with the value of  $G(\text{H}_2) = 0.42$  for NaCl-saturated solutions in the range 0 to 85°C stated by Spitsyn et al.<sup>1</sup> The higher values for  $G(\text{H}_2)$  in brine (~2) inferred by Jenks<sup>2</sup> from results with KCl solutions reported by previous Russian workers are completely discounted.

Our conclusions regarding the effects of 5 to 8% air on the values for  $G(\text{H}_2)$  apparently do not agree with the stated findings

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of Spitsyn et al. that the value for  $G(H_2)$  in salt solutions is independent of  $O_2$ .

Additionally, we concluded that deaerated solutions containing 10 to 12  $m$   $MgCl_2$  and irradiated at 150 to 180°C exhibit  $G(H_2)$  values greater than those for solutions of lower  $MgCl_2$  concentrations at lower temperatures by factors ranging from 1.0-1.25 at 150-160°C to 1.6-2.0 at 170-180°C. Presumably, the increased hydrolysis of  $MgCl_2$  at higher temperatures and concentrations is responsible for some or all of the increase in  $G(H_2)$ . Also, we found that radiolytic decomposition of the water of hydration in crystals of  $MgCl_2 \cdot 6H_2O$  takes place, but that the effective values for  $G(H_2)$  are much less than those in a liquefied solution with the same ratio of  $MgCl_2$  to  $H_2O$ . Most of the  $H_2$  is not released from the crystals until the irradiated material is heated above the liquefaction temperature.

Some suggestions for additional experimental work are presented which would help (1) in the identification of the several oxidized species that are apparently formed in the radiolysis of brine solutions and (2) in the further clarification of radiolysis in the brines.

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## 1. INTRODUCTION

The work presented in this report comprises an experimental study of certain aspects of the radiation chemistry of NaCl-saturated  $MgCl_2$  solutions and of  $MgCl_2$  hydrates at temperatures in the 30 to 180°C range. The compositions of the solutions and solids employed in the gamma-irradiation experiments and the temperatures of the materials during irradiation are listed in Table 1. The compositions of the selected  $MgCl_2$ -containing solutions are representative of those that might occur in the brines around canisters of solidified high-level wastes or spent fuel from light-water power reactors emplaced in a bedded salt repository. Solution T-1 represents the solutions that would prevail in brines encapsulated within crystals of bedded salt.<sup>3</sup> The compositions of the other  $MgCl_2$ -containing solutions represent some of the materials that would be formed if brine inclusions of the approximate composition of T-1 became more concentrated by water loss. Water might be lost through evaporation, corrosion, or radiolytic decomposition if the



Table 1. Compositions and temperatures of the solutions and solids employed in gamma-irradiation experiments and reference to data tables

Test solution	Concentration solutes			Temperature during irradiation (°C)	See Table No.
	MgCl <sub>2</sub> (m)	NaBr (m)	NaCl		
T-1	2.4	0.03	sat.	73-85	2
T-1	2.4	0.03	sat.	112-140	4
T-1	2.4	0.03	sat.	30-45	6
T-2	5.8 <sup>a</sup>	0	sat.	30-45	6
T-3	5.8 <sup>a</sup>	b	sat.	75-80	2
T-3	5.8 <sup>a</sup>	b	sat.	106-143	4
T-3	5.8 <sup>a</sup>	b	sat.	30-45	6
S	0	0.05	0	30-45	6
T-3a <sup>c</sup>	10.75	b	sat.	152-160	8
T-3b <sup>c</sup>	9.80	b	sat.	150-160	8
T-3c <sup>c</sup>	11.24	b	sat.	170-180	8
T-3d <sup>c</sup>	11.73	b	sat.	169-182	8
T-3e <sup>c</sup>	9.56	b	sat.	100 <sup>d</sup>	10
T-3f <sup>c</sup>	9.34	b	sat.	100 <sup>d</sup>	10
C-1 <sup>e</sup>	9.26	0	0	80	10
C-2 <sup>e</sup>	9.26	0	0	80	10

<sup>a</sup>Saturated in MgCl<sub>2</sub> at room temperature.

<sup>b</sup>Solution T-3 contained enough NaBr to make 0.08 m in NaBr if all remained in solution.

<sup>c</sup>These highly concentrated solutions were prepared from T-3 through evaporation by heating the solution in the test ampule while purging the gas space with He.

<sup>d</sup>This material was solid during irradiation but was liquefied by heating to 128°C maximum after irradiation.

<sup>e</sup>These solid materials were composed of MgCl<sub>2</sub>·6H<sub>2</sub>O crystals. Ampules containing C-1 were not heated before or after irradiation. After irradiation, ampules containing C-2 were heated to 125°C in a glycerine bath to liquefy the sample and release gases. Liquefaction began at 105°C.

encapsulated brine migrated into spaces immediately adjacent to the canisters in the salt.<sup>3</sup> The irradiation temperatures were also selected to represent those that might occur around waste canisters in a salt repository.<sup>3</sup>

A principal objective of this experimental work was to establish the values for the yield of  $H_2$  [ $G(H_2)$ ] in the gamma-ray radiolysis of the concentrated brines that might occur in waste repositories in salt. The yield of  $H_2$  is of prime significance since  $H_2$  is the only stable, reduced species that can be formed in the radiolysis of brine solutions. Data available when this work was started<sup>2,3</sup> indicated values for  $G(H_2)$  between  $\sim 0.45$  and  $2.1$  at exposure temperatures of  $\sim 25^\circ C$ . We aimed at establishing the values for  $G(H_2)$  within closer limits and over a range of temperatures up to  $\sim 180^\circ C$ .\*

Another objective of the experimental work was to identify the oxidized species that must be formed along with radiolytic  $H_2$ . In pure water, these species would consist of either  $O_2$  or  $H_2O_2$  or both. These same species and many others are conceivable in the radiolysis of brines. However, previously reported theoretical analyses<sup>2,3</sup> indicate that the most likely species in brines are  $O_2$ ,  $ClO_3^-$ , and either  $H_2O_2$  or  $Cl_2$ , and accordingly these species were sought.

An additional objective of this work was to obtain information on the possible radiolytic decomposition of water of hydration in hydrates of  $MgCl_2$ .

## 2. EQUIPMENT AND EXPERIMENTAL PROCEDURES

### 2.1 Ampule Description and Procedures

The experiments were conducted using small Pyrex glass ampules in which were sealed the test solution or solid and the test gas atmosphere (Fig. 1). Crystals of  $NaCl$  were also added to the ampules for those experiments in which the test solution was to be saturated in  $NaCl$  during irradiation. The sealed ampules were exposed at a controlled

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\*The results of some recent Russian studies of the radiolysis of  $NaCl$  solutions were published after this present work was completed.<sup>1</sup>

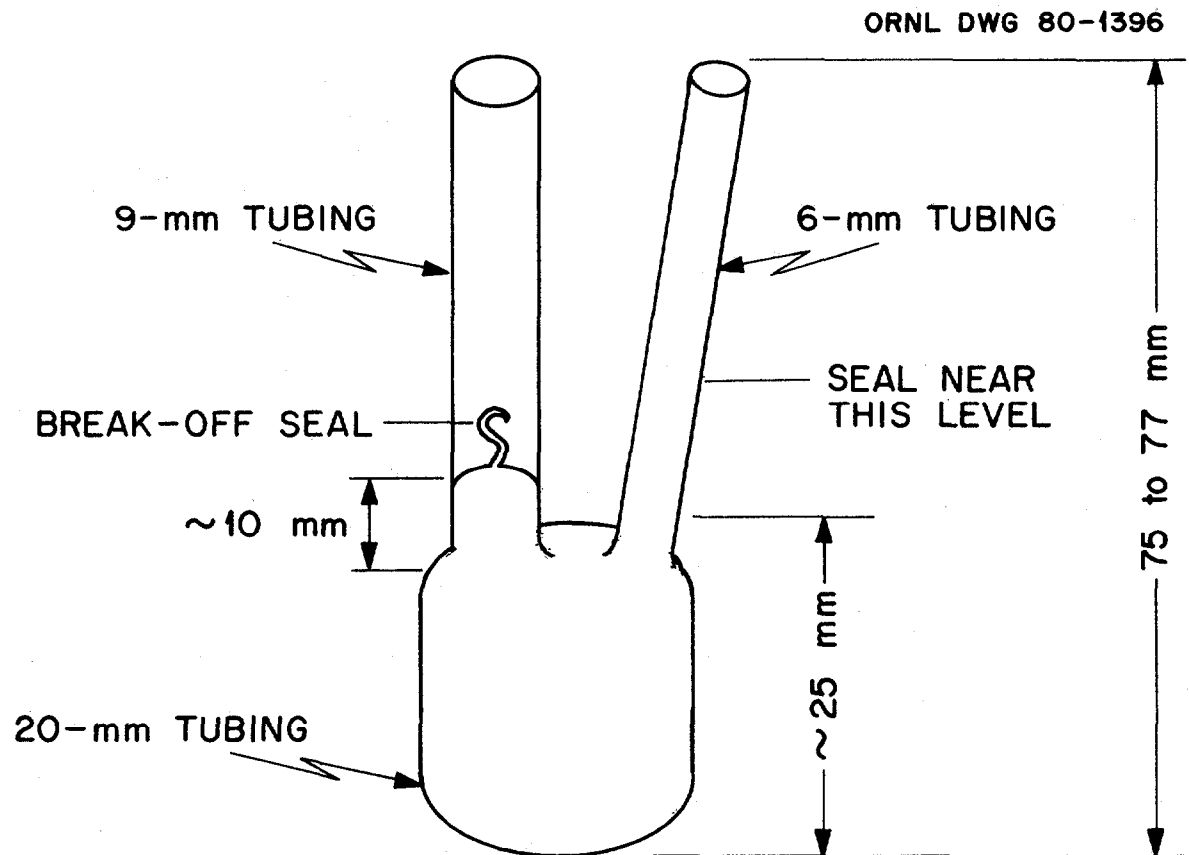


Fig. 1. Glass ampule used in the gamma irradiations.

temperature to gamma rays from a cobalt source available at ORNL. Following irradiation, a standard-taper glass joint was sealed to each ampule. The gas contents of each ampule were then analyzed with a mass spectrometer for fractional concentration of each gaseous species of possible interest. The total amount of gas in each ampule was also measured.

Following these measurements, the ampules were stoppered, stored,\* and then analyzed for  $\text{ClO}_3^-$ ,  $\text{H}_2\text{O}_2$ , or  $\text{Cl}_2$ . Methods of quantitative analysis for micro amounts of these species in concentrated brines, developed by C. S. MacDougall of the ORNL Analytical Chemistry Division as part of this experimental program, have been reported elsewhere.<sup>4</sup>

Ampules of unirradiated control samples were also analyzed. Descriptions of these samples and the conditions and results of the measurements are given in Appendix A.

## 2.2 Cobalt Source

A Shepherd 89-TBq cobalt source was used in all irradiations. The exposure chamber in this source is 150 mm in diameter and 200 mm in height. The chamber is equipped with a removable heater-cooler jacket (electrical resistance heaters and water cooling coils). For the present irradiations, the central part of the jacket was equipped with a thick-walled, cylindrical copper thimble, measuring 30 mm ID, 57.5 mm OD, and 102 mm high, and having a 9.0-mm-thick bottom. The vertical copper walls contained two drilled thermocouple wells. A capped nickel thimble containing the sealed glass ampule of the test solution or solid fitted within the copper thimble to complete the assembly. The nickel thimble was 25 mm OD x 86 mm high, with 0.89-mm-thick vertical walls and a 1.0-mm-thick bottom. The nickel cap was 14 mm thick and was connected by a 1.5-mm-ID tube to the house off-gas system. A slow stream of air was drawn through this line whenever an ampule was being heated or irradiated.

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\*The ampules were stored in the dark after irradiation and prior to the mass spectrometer measurements, except during the sealing-on of the standard-taper joint. Subsequent to the mass spectrometer measurements, the ampules were exposed to the light in the laboratory.

The purpose of the heavy copper thimble was to ensure uniformity of temperature within the ampule. The air sweep to the off-gas system was provided as a means of removing water vapor and gases in the event of ampule rupture. Temperature in the copper thimble at 70°C and above was maintained by Variac-controlled adjustments in the electrical power to the heater jacket. Temperatures of 30 to 45°C in the thimble were achieved by passing tap water through the cooling coils of the jacket.

### 2.3 Gamma-Ray Dose Rate

The gamma-ray dose rate in water at the ampule-irradiation site in the cobalt source was determined using brief irradiations of an ~500-μM ceric sulfate dosimeter solution within a 20-mm-ID cylindrical cell equipped with quartz windows 10 mm apart. The cell was lowered into the nickel thimble and irradiated for consecutive periods of several minutes each until the  $\text{Ce}^{4+}$  was exhausted. Measurements of  $\text{Ce}^{4+}$  within the cell solution were made spectrophotometrically. More detailed information on ceric sulfate dosimetry and the procedures and measurements employed in this work is presented in Appendix B.

The results of two different dose rate measurements without water in the coils of the heater-cooler jacket and of one measurement with water in the coils are shown in Fig. 2. The values for change in optical density ( $\Delta\text{OD}$ ) shown by these data correspond to the following values for the rate of energy deposition in water at the irradiation site [ $I_w$ ; see Eq. (B.6), Appendix B]: without water in coils,  $I_w = 8.34 \times 10^{17}$  eV/g  $\text{H}_2\text{O} \cdot \text{min}$ ; with water in coils,  $I_w = 7.96 \times 10^{17}$  eV/g  $\text{H}_2\text{O} \cdot \text{min}$ .

### 2.4 Measurements of Gases within Irradiation and Control Ampules

The irradiated and control ampules were analyzed for gas content and concentration of gas species on a 6-in., 60°-sector focusing mass spectrometer. Each sample ampule was attached to the sample manifold and evacuated. The manifold and ampule were first tested for leaks; then the ampule and a U-shaped trap were immersed in liquid nitrogen. All moisture associated with the sample was frozen because any moisture

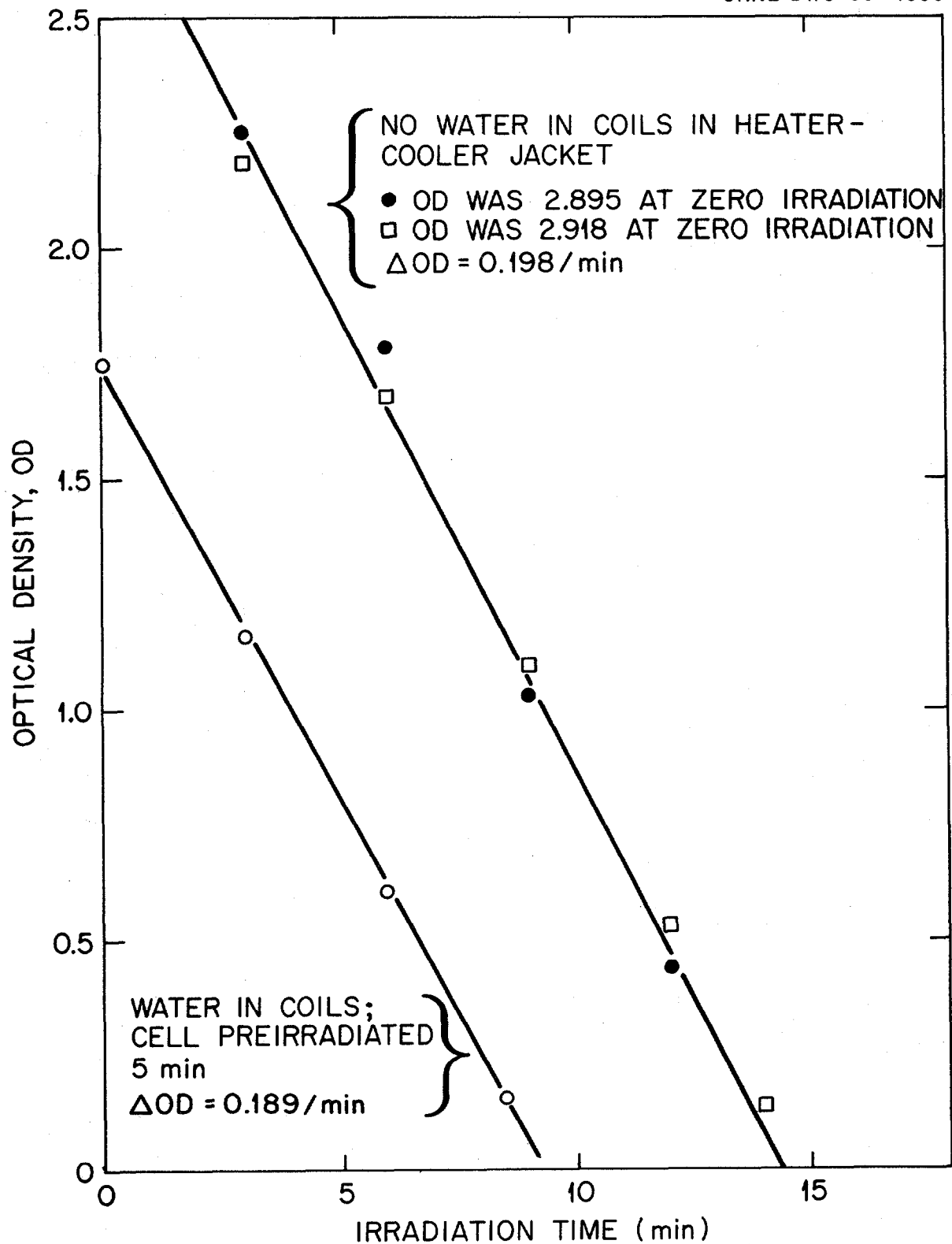


Fig. 2. Results of dose rate measurements with ceric sulfate solution.

in the mass spectrometer could bias the hydrogen and oxygen analysis. Next the glass seal on the ampule was broken, and the total gas pressure was measured on a capacitance manometer (MKS Baratron). The mass spectrometer measurements were then made. The sensitivity of the system was adjusted so that the ion current of He, the predominant gas, would be  $\sim 2 \times 10^{-11}$  A. Then the measurements of other mass species were made. Masses of He, H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, and Ar were usually present. Following the mass analyses, the volume of the gas handling system was determined by expansion of a known amount of He gas into the system. The detailed procedures and calculations used in these measurements are presented in Appendix C.

In a gas mixture, the concentration of any gas having a mono component peak (i.e., a peak not partly due to some other gas) may be calculated from the peak height and the height of the corresponding peak in a calibration run in which the gas pressure and other conditions are suitably controlled. In the calibration run, either a pure gas or a mixture of known composition containing the desired components may be used. The sensitivity is given in terms of peak height per unit of pressure, obtained by dividing the peak height of the component by the partial pressure of the component in the sample reservoir. Sample composition is determined by dividing the mono component peak height by the appropriate sensitivity factor to give its partial pressure. Division by the total pressure in the sample reservoir at the time of analysis then yields the mole percent of the particular component. The following conditions must be satisfied:

1. The ion beam intensity for any component is proportional to the partial pressure of that component in the sample reservoir.
2. The mass spectrum of any component is unaffected by the presence of another component in the sample.
3. The sensitivities of the various components have not changed since the calibration standards were examined.

The calibration gas during these analyses was standard mixture No. H190364, which has the following composition:

<u>Component</u>	<u>mol %</u>
He	30.41
Ar	30.62
N <sub>2</sub>	19.10
H <sub>2</sub>	9.84
CO <sub>2</sub>	5.11
CH <sub>4</sub>	3.02
O <sub>2</sub>	1.89

The estimated accuracies of the mass spectrometer values for H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> in most of the ampules were  $\pm 3\%$  for H<sub>2</sub>,  $< \pm 3\%$  for O<sub>2</sub>, and more accurate for N<sub>2</sub> than for O<sub>2</sub>. For very small concentrations of a gas ( $< 0.01\%$ ), the estimated accuracy was no better than  $\pm 50\%$ .

## 2.5 Preparation of MgCl<sub>2</sub> Test Solutions

The MgCl<sub>2</sub> solutions used in this work were prepared from stockroom supplies of MgCl<sub>2</sub>·6H<sub>2</sub>O (Matheson Coleman & Bell Manufacturing Chemists, #8J31). A stock solution of saturated MgCl<sub>2</sub> was prepared in a 500-mL Pyrex graduated cylinder-flask using a 454-g (1-lb) bottle of MgCl<sub>2</sub>·6H<sub>2</sub>O with an appropriate amount of H<sub>2</sub>O. Helium gas was sparged through the solution for ~15 min to assure saturation and deaerate the solution.

Stock solution T-1 was prepared from the saturated MgCl<sub>2</sub> solution in a 125-mL plastic bottle (Nagle Co.) with deaerated H<sub>2</sub>O, NaCl in excess, and sufficient NaBr to make the composition shown in Table 1.

Solution T-3 was also prepared from the stock MgCl<sub>2</sub> solution in a 125-mL plastic bottle, to which NaCl crystals were added in excess of saturation. NaBr was also added in an amount sufficient to make the solution 0.08 m in Br<sup>-</sup> if all remained in the solution.

Solutions highly concentrated in MgCl<sub>2</sub> were prepared from the T-3 test solution by placing the T-3 solution into an ampule with NaCl crystals and heating the ampule to a high temperature (e.g., 160 or 180°C) while the space over the solution was purged with a slow stream of He. The ampule was weighed periodically; the loss in weight was assumed to represent loss of H<sub>2</sub>O. After the desired loss in weight, the ampule was prepared for irradiation. If the loss of H<sub>2</sub>O exceeded an

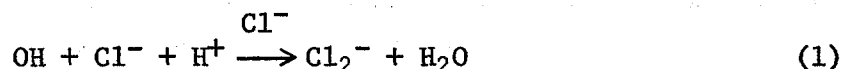


acceptable amount, additional T-3 solution was added to produce the desired concentration of  $\text{MgCl}_2$  at the test temperature.

Other test solutions were made by similar procedures.

## 2.6 Acidity of Test Solutions

It is known that hydrogen ions at sufficiently high concentration can affect the radiolysis of chloride solutions through the following reaction:<sup>2,3</sup>



where  $k = 1.66 \times 10^{10} / \text{M}^2 \cdot \text{s}$ .

Information on the hydrogen ion concentration in the test solutions and on the effects of radiolysis was sought by the following step:

1. Measurements were made of the  $\text{H}^+$  activity in concentrated  $\text{MgCl}_2$  solutions using a  $\text{H}_2$ -Pt electrode with a saturated calomel reference cell. These measurements were made by A. L. Bacarella of the ORNL Chemistry Division.
2. An experimental study was made of the hydrolysis of concentrated  $\text{MgCl}_2$  solutions at room temperature. This work, done by C. F. Baes, Jr. and H. R. Bronstein of the ORNL Chemistry Division, is reported in Appendix D.
3. Nitric acid was added to four different T-1 ampule solutions, which were then irradiated at  $\sim 75^\circ\text{C}$ . Two of these were  $\sim 10 \mu\text{m}$   $\text{HNO}_3$  and two were  $\sim 100 \mu\text{m}$   $\text{HNO}_3$ . The purpose of these experiments was to test the effects of the radiolytic  $\text{HNO}_3$  that might be formed in the gas-vapor phase of an ampule (see Sect. 3.3).

### 3. BACKGROUND INFORMATION BEARING ON THE DESIGN AND INTERPRETATION OF THE IRRADIATION EXPERIMENTS

#### 3.1 Basic Aspects of Radiation Chemistry of H<sub>2</sub>O and Aqueous Solutions

This subject was recently reviewed in ref. 3, and no further discussion is presented in this report. However, the following items are included here for convenient reference.

The presence of Br<sup>-</sup> in the salt-mine brine will inhibit radiation-induced recombination of H<sub>2</sub> and O<sub>2</sub> (or other oxidants) within the solution until the concentration of H<sub>2</sub> reaches a level at least equal to that of the Br<sup>-</sup>. As shown in Table 1, Br<sup>-</sup> was added to most of the test solutions to simulate the compositions that might occur around waste canisters in bedded salt. We believe that our experimental conditions were such that recombination of H<sub>2</sub> and oxidants within our irradiated solutions was negligible.

Values for  $G(\text{H}_2)_w$  were calculated<sup>3</sup> from experimental information using Eqs. (2) and (3):

$$G(\text{H}_2)_w = N_h \cdot (6.02 \times 10^{25}) / M_w \cdot I_s \cdot t \quad (2)$$

and

$$I_s = I_w (1 + E_s/E_w) , \quad (3)$$

where

$N_h$  = number of moles of H<sub>2</sub> found in gas drawn from an irradiated ampule;

$M_w$  = mass of H<sub>2</sub>O within the ampule solution, g;

$t$  = time that ampule was irradiated, min;

$I_s$  = rate of deposition of gamma-ray energy in H<sub>2</sub>O in brine solution, eV/min·g of H<sub>2</sub>O;

$I_w$  = rate of deposition of gamma-ray energy in H<sub>2</sub>O at location of brine, eV/min·g of H<sub>2</sub>O;

$E_s/E_w$  = the ratio of the number of orbital electrons associated with the solutes dissolved in a given mass of H<sub>2</sub>O to the

number of orbital electrons associated with the given mass of H<sub>2</sub>O solvent.

In the expression " $G(\text{H}_2)_w$ ," the subscript "w" is to emphasize the fact that allowances were not made for the possibilities of gas-phase reactions in the evaluations indicated in Eqs. (2) and (3).

### 3.2 Radiation-Induced Combination of H<sub>2</sub> and O<sub>2</sub> to Form H<sub>2</sub>O in the Gas-Vapor Phase

This topic was also reviewed in ref. 3. Briefly, it is known that this gas-vapor phase radiolytic reaction does take place. The values for  $G(\text{H}_2\text{O})_v^*$  in the particular gas-vapor compositions used in our work have not been determined. However, estimates of the maximum values for  $G(\text{H}_2\text{O})_v$  [equal to  $G(-\text{H}_2)_v^{**}$ ] in our gas-vapor mixtures can be made from the results of work reported by Lind and coworkers<sup>5-7</sup> with mixtures of H<sub>2</sub>, O<sub>2</sub>, water vapor, and Ar at the range of test temperatures employed in this present work. The maximum values for  $G(-\text{H}_2)_v$  thus estimated were 10, 15, 18, and 21 at 30 to 100°C, 112 to 140°C, 160°C, and 180°C, respectively. In using these  $G$  values, we assumed that all radiation energy absorbed in the gas-vapor mixture contributed equally to the formation of H<sub>2</sub>O, regardless of the gas-vapor in which the energy was absorbed.

Possible effects of back reactions in the vapor phase on the observed values for  $G(\text{H}_2)_w$  were estimated from the values for the ratio  $R_1$ :

$$R_1 = \frac{G(-\text{H}_2)_v \cdot M_v}{G(\text{H}_2)_w \cdot \alpha \cdot M_w \cdot 10^6}, \quad (4)$$

---

\*The subscript "v" signifies that the quantities and processes represented take place in a gas-vapor region.

\*\*The negative sign in " $G(-\text{H}_2)_v$ " signifies that the  $G$  value refers to processes in which H<sub>2</sub> is consumed by reaction with O<sub>2</sub> to form H<sub>2</sub>O.

where

$M_v$  = total mass of gases and vapor in the gas-vapor phase of an ampule during irradiation,  $\mu\text{g}$ ;

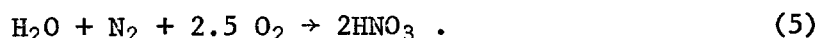
$M_w$  = mass of  $\text{H}_2\text{O}$  within the solution during irradiation, g;

$\alpha = 1 + E_s/E_w$  (see ref. 3).

Direct experimental tests of possible effects on  $G(\text{H}_2)_w$  of gas-phase reactions were made using different relative volumes of solution and gas phases and thus different values for the ratio  $M_v/\alpha \cdot M_w$  in different ampules irradiated at a given temperatures. The presence or absence of effects of gas phase reactions on  $G(\text{H}_2)_w$  were then evaluated using Eq. (4) along with experimental data.

### 3.3 Radiation-Induced Formation of $\text{HNO}_3$ in Gas-Vapor Phase

This topic was also recently reviewed in ref. 3. It is known that some  $\text{HNO}_3$  and/or other nitrogen oxides may form in moist air under irradiation.<sup>8,9</sup> The available evidence indicates that  $\text{HNO}_3$  is formed initially at a  $G$  value in the range of 1 to 3, and that formation continues until the  $\text{H}_2\text{O}$  vapor is exhausted. Nitrogen dioxide ( $\text{NO}_2$ ) is then formed, and no further  $\text{HNO}_3$  is produced in the presence of  $\text{NO}_2$ . The radiolytic reaction that forms  $\text{HNO}_3$  is believed to be



The available evidence also indicates that nitrous oxide is formed in addition to  $\text{HNO}_3$  and that this formation is independent of  $\text{H}_2\text{O}$  vapor. The reported values for  $G(\text{N}_2\text{O})$  were about 1.0 at the start of an irradiation, decreasing with increasing dose to an asymptotic value of 0.55.

Estimates of the maximum concentration of  $\text{HNO}_3$  in our irradiated solutions which could result from the gas-phase formation of  $\text{HNO}_3$  were made using the general approach described in Sect. 3.2. It was assumed that  $G(\text{HNO}_3)_v$  equaled 3.0 and that all radiation energy absorbed in the gas-vapor mixture contributed equally to the formation of  $\text{HNO}_3$ , regardless of the gas or vapor in which the energy was absorbed. The maximum concentrations thus estimated ranged from about 7.0  $\mu\text{m}$  at the lowest

irradiation temperature (30-45°C) to about 60  $\mu\text{m}$  at the highest irradiation temperature (180°C). The values at intermediate temperatures were about 25  $\mu\text{m}$  at 73 to 85°C and about 40  $\mu\text{m}$  at 112 to 140°C.

The possible maximum effects of  $\text{HNO}_3$  formation on the amount of  $\text{O}_2$  found in an irradiated ampule were estimated as follows:

$$(N_{\text{O}})_{\text{v}} = R_1 \cdot N_{\text{h}} \cdot 1.0 \cdot G(\text{HNO}_3)_{\text{v}} / G(-\text{H}_2)_{\text{v}}, \quad (6)$$

where

$(N_{\text{O}})_{\text{v}}$  = calculated number of moles of  $\text{O}_2$  used in the formation of radiolytic  $\text{HNO}_3$ ;

$R_1$  = value for the ratio shown by Eq. (4). [Values for  $R_1$  were calculated in connection with the topic discussed in Sect. 3.2, and it was convenient to use these previously calculated values for the evaluations of  $(N_{\text{O}})_{\text{v}}$ ];

$N_{\text{h}}$  = experimental value for number of moles of radiolytic  $\text{H}_2$  contained in the irradiated ampule;

$G(\text{HNO}_3)_{\text{v}} = 3.0$ ;

$G(-\text{H}_2)_{\text{v}}$  = value for this quantity used in the evaluation of  $R_1$  in Eq. (4).

The possible maximum effects of  $\text{N}_2\text{O}$  formation were estimated by an analogous equation where  $G(\text{HNO}_3)_{\text{v}}$  was replaced by  $G(\text{N}_2\text{O})_{\text{v}} = 1.0$ .

#### 4. EXPERIMENTS AT 73 TO 85°C

##### 4.1 Conditions, Results, and Derived Quantities

Information pertaining to the exposure conditions of ampule-irradiation experiments at these temperatures is set forth in Table 2 together with the analyses of gases after irradiation, and the values for  $G(\text{H}_2)_{\text{w}}$  and  $\text{O}_2$  deficit calculated from the results. The results of postirradiation solution analyses and derived values for equivalent  $\text{O}_2$  are also shown. All irradiation experiments were run in duplicate as indicated by spacing in the table.

Table 2. Exposure conditions, results of gas analyses, and derived quantities for ampules irradiated at 73 to 85°C

Experiment No. and solution	Mass of H <sub>2</sub> O, <i>M<sub>w</sub></i> (g)	Irradiation time (min)	Resulting amount of gases (μmol)					<i>G</i> (H <sub>2</sub> ) <sub><i>w</i></sub> <sup><i>b</i></sup>	Solution analysis results (μmol)		
			Total	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub> deficit <sup><i>a</i></sup>		H <sub>2</sub> O <sub>2</sub>	ClO <sub>3</sub> <sup>-</sup>	Equivalent O <sub>2</sub>
Solution T-1 <sup><i>d</i></sup>											
6 <sup><i>e</i></sup>	0.72	110	208	0.87	2.57	9.72	0.48	0.60		0.009	0.014
14 <sup><i>e</i></sup>	0.79	210	200	1.45	3.64	13.04	0.49	0.48	0.026		0.013
18 <sup><i>e</i></sup>	0.70	210	197	1.34	3.41	11.66	0.40	0.50		0.155	0.233
21	0.64	210	215	1.27	0.34	0.52	0.43	0.51	0.023		0.012
22	0.75	210	205	1.54	0.49	1.07	0.57	0.53	0.001		0.001
23	0.78	110	197	0.75	0.57	1.02	0.08	0.48			
24	0.71	110	204	0.65	0.43	1.04	0.17	0.46		0.028	0.042
27 <sup><i>f</i></sup>	0.83	110	189	0.81	0.59	1.36	0.18	0.49			
28 <sup><i>f</i></sup>	0.86	110	180	0.81	0.43	1.15	0.28	0.47			
33	2.42	20	105	0.42	0.24	0.36	0.07	0.47			
34	2.41	20	99	0.42	0.22	0.33	0.08	0.48	0		0
40 <sup><i>g</i></sup>	2.37	20	94	0.44	0.35	0.90	0.12	0.50	0		0
41 <sup><i>g</i></sup>	2.41	20	119	0.41	0.39	0.87	0.05	0.46		0	0
42 <sup><i>h</i></sup>	2.41	20	84	0.39	0.24	0.35	0.05	0.44	0		0
43 <sup><i>h</i></sup>	2.44	20	84	0.39	0.21	0.33	0.08	0.44			
Solution T-3 <sup><i>d</i></sup>											
19 <sup><i>e</i></sup>	0.70	110	207	0.81	2.94	10.81	0.44	0.51	0		0
20 <sup><i>e</i></sup>	0.71	110	215	0.75	2.09	7.76	0.37	0.48		0.004	0.006
25	0.74	110	185	0.81	0.46	0.94	0.20	0.48	0		0
26	0.77	110	183	0.90	0.53	0.90	0.12	0.51		0.003	0.005

<sup>a</sup>Calculated using Eq. (7).<sup>b</sup>The value of  $G(\text{H}_2)_w$  is that calculated using Eqs. (2) and (3) with  $N_h$  equal to the number of moles of H<sub>2</sub> reported in this table.<sup>c</sup>Values derived from reported results of analyses of irradiated solutions, including adjustment for blank values; ClO<sub>3</sub><sup>-</sup> =  $0.67 \pm 0.10$   $\mu$ g/mL, H<sub>2</sub>O<sub>2</sub> =  $0.15 \pm 0.05$   $\mu$ g/mL (see Appendix A). No adjustments were made to account for the possible presence of some H<sub>2</sub>O<sub>2</sub> in the samples that were analyzed for ClO<sub>3</sub><sup>-</sup> (see ref. 4). No. Cl<sub>2</sub> was detected in any of the irradiated or control samples.<sup>d</sup>See Table 1 for concentrations of solutes. The value of  $\alpha$  [Eq. (4)] at these exposure temperatures was 1.32 for T-1 and 1.49 for T-3.<sup>3</sup><sup>e</sup>These ampules were charged with He during loading by flushing with this gas prior to sealing (loading procedure A). All other ampules described here were charged with He by freezing in liquid nitrogen, then evacuating with a Speedivac Hi Vac pump, backfilling with He, and then thawing and sealing the ampule (loading procedure B).<sup>f</sup>These ampules were submerged in liquid nitrogen starting about 2 h after irradiation. Before transfer to the mass spectroscopy lab, they were removed from the liquid nitrogen and sealed to ground-glass joints in the usual manner. At the mass spectroscopy lab, they were again immersed in liquid nitrogen, where they remained until the gas analyses were completed.<sup>g</sup>HNO<sub>3</sub> added to make solution  $10^{-5}$  M in HNO<sub>3</sub>.<sup>h</sup>HNO<sub>3</sub> added to make solution  $10^{-4}$  M in HNO<sub>3</sub>.

The value for  $O_2$  deficit was calculated as follows:

$$O_2 \text{ deficit} = N_h/2 - (N_o - 0.269 N_n) \quad (7)$$

where the symbols  $N_o$ ,  $N_n$ , and  $N_h$  represent the experimental values for the number of moles of  $O_2$ ,  $N_2$ , and  $H_2$ , respectively, shown by the results of the gas analyses. The  $O_2$  deficit quantity thus calculated represents the deficiency of radiolytic  $O_2$  in an ampule, assuming that the amount of atmospheric  $O_2$  equaled 0.269 times the amount of  $N_2$ .

The listed results of solution analyses have been adjusted for blank amounts of the respective species (see footnote c, Table 2). The value for equivalent  $O_2$  was based on the oxidation-reduction relationships between  $H_2O_2$  and  $O_2$  and between  $ClO_3^-$  and  $O_2$ . These relationships are such that one radiolytic  $ClO_3^-$  is the equivalent of 1.5 radiolytic  $O_2$ , and one radiolytic  $H_2O_2$  is the equivalent of 0.5  $O_2$ . The difference between the values for  $O_2$  deficit and  $O_2$  equivalent in an ampule represents the net deficit of  $O_2$  shown by the experimental results.

Values for the ratio  $R_1$  [Eq. (4)], which were calculated from the data for the experiments with T-1 solutions at these temperatures, are listed in Table 3.

#### 4.2 Discussion

The average value of  $G(H_2)_w$  for all solution T-1 experiments listed in Table 2 except No. 6\* is  $0.487 \pm 0.021$  standard deviation ( $\sigma$ ). There were no significant effects on  $G(H_2)_w$  of differences between methods of filling the ampules, duration of irradiation, or relative volumes of solution and gas-vapor phases in the ampules. There were also no effects of maintaining irradiated ampules at liquid nitrogen temperatures during most of the time interval between completion of irradiation and the mass spectrometer measurements. There were no significant effects on  $G(H_2)_w$  of the presence of added 10  $\mu m$  and 100  $\mu m$   $HNO_3$  in experiments 40 through

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\*The value for  $G(H_2)_w$  for experiment No. 6 was excluded from this average because it was far out of line with the other values, it was one of the initial experiments, and the duplicate (No. 5) was a failure.

Table 3. Masses of gases and vapor in some experiments with solution T-1 at 73 to 85°C and probable maximum effects of gas phase combination of H<sub>2</sub> and O<sub>2</sub> on apparent values of  $G(\text{H}_2)_w$

Experiment <sup>a</sup>	Mass of gases and vapor (μg)					Total, $M_v$	$G(\text{H}_2)_w^c$	$R_1^d$
	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	He	H <sub>2</sub> O <sup>b</sup>			
6	1.7	82.2	273	779	916	2052	0.60	0.035
14	2.9	117	365	729	886	2100	0.48	0.042
18	2.7	109	326	722	870	2030	0.50	0.044
21	2.5	10.9	14.6	852	947	1826	0.51	0.042
22	3.1	15.7	30.0	808	909	1686	0.53	0.032
23	1.5	18.2	28.6	779	870	1697	0.48	0.034
24	1.3	13.8	29.1	808	909	1759	0.46	0.040
27	1.6	18.9	38.1	761	839	1659	0.49	0.031
28	1.6	13.8	32.2	710	801	1559	0.47	0.029
33	0.84	7.7	10.1	416	466	901	0.47	0.006
34	0.84	7.0	9.2	392	439	848	0.48	0.005
40	0.88	11.2	25.2	369	416	823	0.50	0.005
41	0.82	12.5	24.4	469	527	1081	0.46	0.007
42	0.78	7.7	9.8	332	373	723	0.44	0.005
43	0.78	6.7	9.2	331	373	720	0.44	0.005

<sup>a</sup>See Table 1 for composition of solution T-1 and Table 2 for mass of H<sub>2</sub>O in solution in these experiments.

<sup>b</sup>Calculated by employing values for vapor pressure of NaCl-saturated MgCl<sub>2</sub> solutions at 80°C in ref. 3.

<sup>c</sup>See Table 2 and Sect. 3.1.

<sup>d</sup>See Eq. (4). The yield for recombination of H<sub>2</sub> and O<sub>2</sub> to form H<sub>2</sub>O in the gas-vapor phase [ $G(-\text{H}_2)_v = 10$ ] was based on values for  $M(\text{H}_2\text{O})/N$  in refs. 5-7 and on the assumptions that  $W$  (energy expended to form an ion pair) equaled 35 eV/ $N$  in the gas-vapor mixture and that all ion pairs formed there contributed equally to H<sub>2</sub>O formation, regardless of the gas-species which was ionized. For solution T-1,  $\alpha = (1 + E_s/E_w) = 1.32$ .



43. Nor were there any significant differences between values for  $G(\text{H}_2)_w$  in the T-3 and T-1 solutions.

The values for  $R_1$  listed in Table 3 indicate a maximum possible effect of  $\sim 4\%$  on  $G(\text{H}_2)_w$  resulting from radiation-induced formation of  $\text{H}_2\text{O}$  from  $\text{H}_2$  and  $\text{O}_2$  in the gas-vapor phase. However, the experimental values for  $G(\text{H}_2)_w$  showed no significant difference between experiments with  $R_1 = 0.044$  and those with  $R_1 = 0.005$ , indicating no effects of gas phase formation of  $\text{H}_2\text{O}$  on  $G(\text{H}_2)_w$ . These considerations led to the tentative conclusion that  $G(\text{H}_2)_w$  equaled  $G(\text{H}_2)$  in the experiments at these temperatures.

The available experimental results listed in Table 2 provided definite evidence for the presence of small amounts of  $\text{ClO}_3^-$  and  $\text{H}_2\text{O}_2$  in some of the ampules. The largest amount of  $\text{ClO}_3^-$ , found in the solution from experiment No. 18, represented about 35% of the oxidant that would be formed along with the  $1.34 \mu\text{mol}$  of  $\text{H}_2$  found in the irradiated ampule. The amounts of  $\text{H}_2\text{O}_2$ , in terms of equivalent  $\text{O}_2$ , were less than the amounts of  $\text{ClO}_3^-$  in similar experiments. No  $\text{Cl}_2$  was detected in any of the solutions. It should be noted that these solutions were stored for several months at room temperature before the solution analyses were made, and it is conceivable that some changes in  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ , and  $\text{ClO}_3^-$  occurred during the storage periods.

The experimental values listed in Table 2 showed that an apparent net deficit of oxidants occurred in each of the ampule experiments. It can be added that estimates of the gas-vapor phase formation of  $\text{HNO}_3$  and  $\text{N}_2\text{O}$  (Sect. 3.3) showed that formation of these species did not contribute significantly to the deficit of oxidants. Possible explanations for the occurrence of the deficits are discussed in Sect. 10.

## 5. EXPERIMENTS AT 100 TO 143°C

Tables 4 and 5 present experimental results and quantities derived from experiments at 100 to 143°C. The comments, interpretations and discussions presented in Sect. 4 are generally also applicable to these data. The average value for  $G(\text{H}_2)_w$  for all experiments except Nos. 7 and 8 was  $0.477 \pm 0.020 \sigma$ . This value is very near that found for those

Table 4. Exposure conditions, results of gas analyses, and derived quantities  
for ampules irradiated at 100 to 143°C

Experiment No. and solution <sup>a</sup>	Temperature (°C)	Mass H <sub>2</sub> O, <i>M</i> <sub>w</sub> (g)	Irradiation time (min)	Resulting amount of gases (μmol)					Solution analysis results (μmol)			
				Total	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub> deficit	<i>G</i> (H <sub>2</sub> ) <sub>w</sub>	H <sub>2</sub> O <sub>2</sub>	ClO <sub>3</sub> <sup>-</sup>	Equivalent O <sub>2</sub>
Solution T-1												
7 <sup>b</sup>	100-124	0.71	110	207	0.89	3.11	11.96	0.55	0.62	0		0
8 <sup>b</sup>	116-123	0.68	110	216	0.91	2.51	9.89	0.61	0.66			
29	117-140	0.84	55	183	0.42	0.27	0.35	0.03	0.49	0		0
30	132-108	0.80	55	167	0.41	0.15	0.30	0.13	0.50	0		0
35	112-117	2.46	20	93	0.41	0.20	0.33	0.09	0.45		0	0
36	115-118	2.44	20	93	0.43	0.19	0.33	0.12	0.47	0		0
Solution T-3												
31	106-143	0.81	55	167	0.45	0.22	0.27	0.08	0.49	0		0
32	139-143	0.84	55	169	0.44	0.19	0.32	0.07	0.46			

<sup>a</sup>The estimated values of  $\alpha$  ( $= 1 + E_s/E_w$ ) at these temperatures were 1.34 for T-1 and 1.50 for T-3.<sup>3</sup>

<sup>b</sup>Loading procedure A; ampules for all other experiments listed here were prepared by loading procedure B.

Table 5. Masses of gases and vapor in some experiments with solution T-1 at 100 to 140°C, and probable maximum effects of gas phase combination of H<sub>2</sub> and O<sub>2</sub> on apparent values of  $G(\text{H}_2)_w$

Experiment	Mass of gases and vapor (μg)					Total, $M_v$	$G(\text{H}_2)_w$	$R_1^b$
	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	He	H <sub>2</sub> O <sup>a</sup>			
7	1.8	99.5	335	764	4792	6014	0.62	0.15
8	1.8	80.3	227	811	5001	6193	0.66	0.15
29	0.9	8.6	9.8	727	4237	5001	0.49	0.14
30	0.8	4.8	8.4	665	3866	4561	0.50	0.14
35	0.8	6.4	9.2	368	2154	2547	0.45	0.025
36	0.9	6.1	9.2	368	2154	2547	0.47	0.025

<sup>a</sup>Calculated by employing values for vapor pressure of NaCl-saturated MgCl<sub>2</sub> solutions at 130°C in ref. 3.

<sup>b</sup>See Eq. (4);  $G(-\text{H}_2)_v = 15$ , calculated by the method explained in footnote d, Table 3;  $\alpha = (1 + E_s/E_w) = 1.34$  for the test solution.

experiments at 73 to 85°C that employed the same loading procedures. However, the average value of 0.64 for  $G(\text{H}_2)_w$  for Nos. 7 and 8 is significantly greater than the average for the other experiments. The ampules for these two experiments were prepared using loading procedure A (see footnote e, Table 2), and the analyses showed that they contained more air than the other ampules, which were prepared using loading procedure B (see Sect. 10).

## 6. EXPERIMENTS AT 30 TO 45°C

Information presented in Tables 6 and 7 regarding experiments at 30 to 45°C is analogous to that presented in previous sections. The test solutions employed with experiment Nos. 46 and 47 were 0.05 m in NaBr and contained no other solute.

Comments, interpretations and discussions presented in Sects. 4 and 5 are generally applicable also to data from these experiments.

The average value for  $G(\text{H}_2)_w$  for all experiments in which the ampules were prepared using loading procedure B (see footnote e, Table 2) was  $0.435 \pm 0.029 \sigma$ . This value is less than the average values of 0.487 and 0.477 for  $G(\text{H}_2)_w$  at 73 to 85°C and 106 to 143°C, respectively, but there is an overlap at the extremes of the standard errors.

Possible explanations for the apparently higher values for  $G(\text{H}_2)_w$  observed with the other ampules prepared using loading procedure A are considered in Sect. 10.

The most probable explanation for the apparently low value for  $G(\text{H}_2)_w$  for the 0.05 m NaBr solutions is that some condensation of vapor occurred during irradiation on the walls of the ampules, which were in contact with the gas-vapor phase. Rapid, radiation-induced combination would take place between  $\text{H}_2$  and  $\text{O}_2$  dissolved in this condensate because scavenger  $\text{Br}^-$  would be absent. (No condensation was expected in ampules loaded with either T-1 or T-3 test solutions because the vapor pressure of these solutions at a given temperature is appreciably less than that of pure  $\text{H}_2\text{O}$ .)<sup>3</sup>

Table 6. Exposure conditions, results of gas analyses, and derived quantities for ampules irradiated at 30 to 45°C

Experiment No. and solution	Mass of H <sub>2</sub> O, $M_w$ (g)	Irradiation time (min)	Resulting amount of gases ( $\mu$ mol)					$G(H_2)_w$	Solution analysis results ( $\mu$ mol)		
			Total	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub> deficit		H <sub>2</sub> O <sub>2</sub>	ClO <sub>3</sub> <sup>-</sup>	Equivalent O <sub>2</sub>
Solution T-1 <sup>a</sup>											
12 <sup>b</sup>	0.73	110	208	0.83	1.91	7.09	0.41	0.61	0		0
13 <sup>b</sup>	0.73	110	215	0.73	2.51	9.35	0.37	0.53		0	
44	2.40	30	106	0.52	0.29	0.38	0.08	0.42		0	0
45	2.28	30	119	0.56	0.25	0.40	0.14	0.48			
52	1.93	30	140	0.41	0.22	0.39	0.08	0.42	0		0
53	1.98	30	129	0.43	0.19	0.33	0.11	0.43		0.004	0.006
Solution T-2 <sup>a</sup>											
16 <sup>b,c</sup>	0.65	110	204	0.98	3.22	12.48	0.63	0.71	0		0
17 <sup>b,c</sup>	0.71	110	206	0.97	2.86	10.84	0.54	0.64		0.046	0.069
Solution T-3 <sup>a</sup>											
58	1.53	30	143	0.40	0.17	0.23	0.09	0.45		0.041	0.062
59	1.47	30	164	0.36	0.16	0.23	0.08	0.45			
62	1.41	30	122	0.32	8.67	24.69	-1.87	0.39			
Solution S <sup>a</sup>											
46	2.27	30									
47	2.17	30	144	0.22	0.86	1.06	-0.46	0.26	0.006		0.003

<sup>a</sup>See Table 1 for concentrations of solutes. The estimated value of  $\alpha$  ( $= 1 + E_s/E_w$ ) at these temperatures was 1.31 for T-1 and 1.49 for T-3.<sup>3</sup>

<sup>b</sup>Loading procedure A; ampules for other experiments listed here were prepared by loading procedure B.

<sup>c</sup>The solution used in these ampules contained no NaBr but otherwise was the same as T-3.

Table 7. Masses of gases and vapor in some experiments with solution T-1 at 30 to 45°C, and probable maximum effects of gas phase combination of H<sub>2</sub> and O<sub>2</sub> on apparent values of  $G(\text{H}_2)_w$

Experiment	Mass of gases and vapor ( $\mu\text{g}$ )					Total, $M_v$	$G(\text{H}_2)_w$	$R_1^b$
	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	He	H <sub>2</sub> O <sup>a</sup>			
12	1.7	61.1	194	793	153	1207	0.61	0.021
13	1.5	80.3	262	810	158	1185	0.53	0.023
44	1.0	9.3	10.6	419	78	518	0.42	0.004
45	1.1	8.0	11.2	471	88	528	0.48	0.004
52	0.8	7.0	10.9	556	103	678	0.42	0.006
53	0.9	6.1	9.2	512	95	623	0.43	0.006

<sup>a</sup>Calculated by employing values for vapor pressure of NaCl-saturated MgCl<sub>2</sub> solutions at 40°C in ref. 3.

<sup>b</sup>See Eq. (4);  $G(-\text{H}_2)_v = 15$ , calculated by the method explained in footnote d, Table 3;  $\alpha = (1 + E_s/E_w) = 1.31$ .

## 7. EXPERIMENTS AT 150 TO 182°C

Most of the information presented in Tables 8 and 9 regarding experiments at 150 to 182°C is analogous to that presented above except as noted. The comments, interpretations, and discussions in Sect. 4 are generally applicable to these data as well.

The average value of  $G(\text{H}_2)_w$  for the two experiments at 150 to 160°C is 0.50, very near the average value of 0.487 for  $G(\text{H}_2)_w$  at 73 to 85°C (see Sect. 4). However, the average value of  $G(\text{H}_2)_w$  for the two 170 to 182°C experiments is 0.79 and definitely greater than that for the 73 to 80°C experiments mentioned above. Furthermore, the values for the ratio  $R_1$  were quite large, and the possibilities were not excluded that formation of  $\text{H}_2\text{O}$  from  $\text{H}_2$  and  $\text{O}_2$  in the gas-vapor phase was sufficient to lower significantly the values of  $G(\text{H}_2)_w$ . If we assume that this fractional lowering was equal to the value of  $R_1$  in each of these experiments, the actual average values for  $G(\text{H}_2)$  were 1.05 and 0.62 in the 170 to 182°C and 150 to 160°C experiments, respectively.

8. EXPERIMENTS WITH SOLID  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  AT 80 AND 100°C

Conditions and results of experiments with solid  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  at 80 and 100°C are presented in Table 10. Experimental methods and procedures for calculating derived quantities are analogous to those already described.

The results of experiment Nos. 77 and 78 showed that the value of  $G(\text{H}_2)_w$  for the solid crystals of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is significant but only about one-fourth of that found with T-1 and T-3 solutions at the same temperature. The other experiments with crystals of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , experiment Nos. 73 and 74, were not liquefied after irradiation, and they showed negligible amounts of  $\text{H}_2$ . It can be tentatively concluded that the radiolysis products remained trapped within the crystals and that the gases were released upon liquefying the samples.

The values of  $G(\text{H}_2)_w$  for experiment Nos. 60 and 61, which were irradiated at 100°C, were about 2.5 times greater than those for experiment Nos. 77 and 78. As noted in footnote *d*, Table 10, solutions T-3e

Table 8. Exposure conditions, results of gas analyses, and derived quantities for ampules irradiated at 160 to 182°C

Experiment	Solution <sup>a</sup>	$\alpha$ ( $=1+E_s/E_w$ )	Mass of H <sub>2</sub> O, $M_w$ (g)	Irradiation time (min)	Resulting amount of gases ( $\mu$ mol)					
					Total	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub> deficit	$G(H_2)_w$
37	T-3a	1.87	1.26	30	116	0.45	0.05	0.20	0.23	0.46
38	T-3b	1.81	1.37	50	121	0.92	0.15	0.67	0.49	0.54
56	T-3c	1.93	1.06	30	161	0.76	0.02	0.08	0.41	0.89
57	T-3d	1.98	1.05	30	163	0.59	<0.02	0.11	0.35	0.68

<sup>a</sup>See Sect. 2.6 for information on preparation of these concentrated solutions from solution T-3. These ampules were charged with He by evacuating for 2 min, backfilling with He, and then sealing. The ampules were not submerged in liquid nitrogen during evacuation since it was established that no detectable loss of weight from the material (solid at room temperature) took place during the 2-min evacuation. See Table 1 for concentration of solutes and temperatures during irradiation.



Table 9. Masses of gases and vapor in some experiments at 160 to 182°C with solutions derived from T-3, and probable maximum effects of gas phase combination of H<sub>2</sub> and O<sub>2</sub> on apparent value of  $G(H_2)_w$

Experiment	$\alpha \cdot M_w$ (g) <sup>w</sup>	Mass of gases and vapor ( $\mu$ g)					Total, $M_v$	$G(H_2)_w$	$G(-H_2)_v^b$	$R_1^c$
		H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	He	H <sub>2</sub> O <sup>a</sup>				
37	2.36	0.9	1.6	5.6	461	1014	1483	0.46	18	0.23
38	2.48	1.8	4.8	18.8	477	1359	1861	0.54	18	0.25
56	2.05	1.5	0.6	2.2	641	2027	2672	0.89	21	0.31
57	2.08	1.2	<0.6	3.1	649	1732	2385	0.68	21	0.35

<sup>a</sup>Calculated by employing values for vapor pressure of NaCl-saturated MgCl<sub>2</sub> solutions in ref. 3.

<sup>b</sup>This quantity is the yield for recombination of H<sub>2</sub> and O<sub>2</sub> to form H<sub>2</sub>O in the gas-vapor phase. The listed values were estimated on the bases of values for  $M(H_2O)/N$  in refs. 5-7, and on the assumptions that  $W$  (energy expended to form an ion pair) equaled 35 eV/ $N$  in the gas-vapor mixture and that all ion pairs formed there contributed equally to H<sub>2</sub>O formation, regardless of the gas species that was ionized.

<sup>c</sup>See Eq. (4).

Table 10. Exposure condition, results of gas and solid analyses, and derived quantities for irradiation experiments with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  at 80 and 100°C

Experiment	Solution <sup>a</sup>	Mass of $\text{H}_2\text{O}$ , $M_w$ (g)	Irradiation time (min)	Resulting amount of gases ( $\mu\text{mol}$ )				$G(\text{H}_2)_w^b$	Solution analysis results <sup>c</sup> ( $\mu\text{mol}$ )		
				Total	$\text{H}_2$	$\text{O}_2$	$\text{N}_2$		$\text{H}_2\text{O}_2$	$\text{ClO}_3^-$	Equivalent $\text{O}_2$
60	T-3e <sup>d</sup>	1.47	30	129	0.25	8.47	21.5	0.23	0		0
61	T-3f <sup>d</sup>	1.47	30	139	0.26	9.25	26.4	0.24			
73	C-1	0.45	50	210	0.004	0.004	0.015	Neg.		0.012 <sup>e</sup>	0.018
74	C-1	0.51	50	186		0.004	0.015		0.006		0.003
77	C-2	1.20	50	176	0.13	0.019	0.107	0.09			
78	C-2	1.09	50	178	0.13	0.027	0.161	0.10			

<sup>a</sup>See Table 1 for compositions, irradiation temperatures, and ampule-handling procedures.

<sup>b</sup>The assumed value of  $E_s/E_w$  for the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was 0.77 (see ref. 3).

<sup>c</sup>The solid was dissolved in the amount of  $\text{H}_2\text{O}$  required to yield a saturated solution of  $\text{MgCl}_2$  at 25°C. The resulting solution was analyzed for  $\text{H}_2\text{O}_2$  or  $\text{ClO}_3^-$ , as indicated, and the results were treated as described in footnote c, Table 2.

<sup>d</sup>These ampule samples were prepared and treated as follows: place test solution T-3 in ampule, start sweep of He through gas phase, and heat ampule in sand bath to about 150°C maximum. Cool and weigh ampule, and add additional T-3 as needed to make ratio of  $\text{MgCl}_2$  to  $\text{H}_2\text{O}$  close to 1:6 (equivalent to that in a 9.26  $\mu$   $\text{MgCl}_2$  solution). Solution T-3e was the equivalent of 9.56  $\mu$   $\text{MgCl}_2$ ; solution T-3f was the equivalent of 9.34  $\mu$   $\text{MgCl}_2$ . Attach ampule to vacuum system, freeze, evacuate, backfill with He from reservoir, warm, and seal ampule. Heat ampule in glycerine bath to about 140°C to liquefy and homogenize sample material. Irradiate; then heat in glycerine bath to 128°C maximum to liquefy sample and release gases (the irradiated samples started to liquefy at 100°C during this heating step), and send sample to mass spectrometry laboratory.

<sup>e</sup>The stoichiometric amount of  $\text{H}_2$  which must have accompanied this amount of  $\text{ClO}_3^-$  would correspond to 0.07 for  $G(\text{H}_2)$  in this experiment.

and T-3f started to liquefy at  $\sim 100^\circ\text{C}$  during the heating subsequent to irradiation. Accordingly, it is possible that liquid was present during irradiation and that this liquid was responsible for the relative high values for  $G(\text{H}_2)_w$ . It is also conceivable that the differences between the sample materials was responsible for the observed difference between values for  $G(\text{H}_2)_w$ ; samples T-3e and T-3F comprised at least initially a single competent solid, whereas C-2 was composed of many fine crystals.

### 9. THE ACIDITY OF $\text{MgCl}_2$ SOLUTIONS

The results of measurement by A. L. Bacarella<sup>10</sup> of the activity of  $\text{H}^+$  in several  $\text{MgCl}_2$  solutions at  $30^\circ\text{C}$  are set out in the following tabulation:

Solution composition	$\text{H}^+$ activity	
	$\mu\text{molar}$	$\mu\text{molal}$
2.50 $\underline{\text{m}}$ $\text{MgCl}_2^a$	100	110
5.83 $\underline{\text{m}}$ $\text{MgCl}_2^b$	400	520
2.4 $\underline{\text{m}}$ $\text{MgCl}_2^a$ saturated NaCl, 100 $\underline{\mu\text{m}}$ $\text{HNO}_3$	320	370

<sup>a</sup>Prepared by diluting saturated solution of  $\text{MgCl}_2$  (MCB,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , batch #8j31).

<sup>b</sup>Saturated  $\text{MgCl}_2$  (Fisher,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , lot #701153).

Measurements were made with a  $\text{H}_2$ -Pt electrode; the reference electrode was saturated calomel in saturated KCl. No corrections were made or attempted for the possible presence of junction potentials in the emf cell. However, it is believed that these potentials were not large and had negligible effects ( $\sim 12\%$ ) on the results either with the solution composition measured and with saturated KCl in the reference electrode.

These activity values are much greater than the concentration of  $\text{H}^+$  that would be expected from hydrolysis as predicted from the results of Bronstein and Baes reported in Appendix D. For example, an  $\text{H}^+$  concentration of 3.2  $\underline{\mu\text{m}}$  due to hydrolysis in a saturated solution of  $\text{MgCl}_2$  can be calculated from the equations in Appendix D. Although the

activity of  $H^+$  would be expected to be much greater than the concentration, a factor of about 100 seems unreasonably high (Appendix E). It is likely that the  $MgCl_2 \cdot 6H_2O$  from which these solutions were made was contaminated with a small amount of HCl or some other source of  $H^+$ .

We believe that the  $H^+$  contaminations in the test solutions were below the levels at which significant effects on the radiolytic characteristics of the solutions would take place.

## 10. DISCUSSIONS

Discussions of most of the experimental data and pertinent theoretical information have been presented in previous sections of this report. This section contains summaries of certain important aspects of the experimental data and discussions of the possibilities that radiolytic  $Cl_2$  accounted for observed deficits of  $O_2$  and for effects of loading procedure on values for  $G(H_2)_w$ .

Table 11 lists average values for  $G(H_2)_w$  and  $G(O_2)_w$ , which were derived from the experimental data for brine solutions listed in Tables 2, 4, 6, and 8. It can be noted that the experimental values for  $G(O_2)_w$  are related to other quantities discussed here according to the following equation:

$$2G(O_2)_w = G(H_2)_w [1 - 2(O_2 \text{ deficit})/N_h] . \quad (8)$$

### 10.1 The Relationship between $G(H_2)_w$ and $G(H_2)$ and Factors That Might Affect the Relationship

As stated in preceding sections,  $G(H_2)_w$  is defined as the apparent yield of  $H_2$  calculated directly using experimental data for the amount of  $H_2O$  in the ampule and the gamma-ray dose to the  $H_2O$ . Similarly, the quantity  $G(H_2)$  represents the yield of  $H_2$  shown by the experimental data after making allowances for the occurrence of any gas-phase reactions that might either remove  $H_2$  by chemical reaction or affect the chemistry of the solution in such a manner as to alter the net rate of formation of radiolytic  $H_2$ . For convenience in discussion,  $\delta$  represents the ratio of  $G(H_2)$  to  $G(H_2)_w$  (i.e.,  $G(H_2)/G(H_2)_w = \delta$ ).

Table 11. Average of experimental values for  $G(H_2)_w$  and  $G(O_2)_w$  in NaCl-saturated  $MgCl_2$  solutions

Temperature during irradiation (°C)	$MgCl_2$ concentrations (m)	Data in table No.	Experimental value for $G(H_2)_w$ with indicated ampule-loading procedure <sup>a</sup>			Experimental value for $G(O_2)_w$ with indicated ampule-loading procedure <sup>a</sup>		
			A	B	Other	A	B	Other
30-45	2.4, 5.8	6, 7	$0.62 \pm 0.07^b$	$0.44 \pm 0.03^b$		$0.00^c$	$0.13 \pm 0.01^b$	
73-85	2.4, 5.8	2, 3	$0.49 \pm 0.01^b$	$0.49 \pm 0.02^b$		$0.05 \pm 0.05^b$	$0.13 \pm 0.04^b$	
100-143	2.4, 5.8	4, 5	$0.64 \pm 0.02^d$	$0.48 \pm 0.02^b$		$0.00^e$	$0.14 \pm 0.04^b$	
150-160	10.8, 9.8	8, 9			$0.50 \pm 0.04^d (0.62)^f$			$0.00^e$
169-182	11.2, 11.7	8, 9			$0.79 \pm 0.10^d (1.05)^g$			$0.00^e$

<sup>a</sup>See Table 2, footnote e.

<sup>b</sup>Standard deviation.

<sup>c</sup>Value from four experiments none of which was significantly greater than zero. The result from experiment No. 62 was disregarded because the  $O_2$  value was inordinately high.

<sup>d</sup>Spread of results from two samples.

<sup>e</sup>Value from two experiments, neither of which was greater than zero.

<sup>f</sup>Average of observed values increased by factor of 1.24, which would be appropriate if formation of  $H_2O$  from  $H_2$  and  $O_2$  in the gas-vapor phase took place with an assumed maximum value for  $G(H_2O)_v = 18$  (see Table 9).

<sup>g</sup>Average of observed values increased by factor of 1.33, which would be appropriate if formation of  $H_2O$  from  $H_2$  and  $O_2$  in the gas-vapor phase took place with an assumed maximum value for  $G(H_2O)_v = 21$  (see Table 9).

The definitions for  $G(O_2)_w$  and  $G(O_2)$  are analogous to those for  $G(H_2)_w$  and  $G(H_2)$ .

The conceivably significant gas phase reactions that were recognized at the start of this work and that were tested for effects on  $\delta$  were (1) radiation-induced formation of  $H_2O$  from  $H_2$  and  $O_2$  in the gas phase and (2) radiation-induced formation of  $HNO_3$  and other oxides of nitrogen in the gas phase. We have now considered the possibilities that  $Cl_2$  was also a radiolytic product and that gas phase reactions between  $H_2$  and  $Cl_2$  to form  $HCl$  affected some of the results. Experimental and theoretical information bearing on this hypothesis and on the evaluations of  $\delta$  in general are summarized in following sections.

#### 10.2 Apparent Values of $\delta$ in Experiments with NaCl-Saturated Solutions at 30 to 140°C

The large number of experiments with NaCl-saturated  $MgCl_2$  solutions exposed at 73 to 85°C showed no significant effects on the apparent yield of  $H_2$  resulting from differences between the relative volumes of solution and gas-vapor phase in the irradiation ampules or from differences between the durations of irradiation. There were also no effects of adding  $\sim 10$  and  $\sim 100 \mu m$   $HNO_3$  to  $2.4 m$   $MgCl_2$  solutions or of maintaining irradiated ampules at liquid nitrogen temperatures during most of the time interval between completion of irradiation and the mass spectrometer measurement. Finally, no effects resulted from the use of loading procedure A rather than procedure B. These observations led to the tentative conclusions that the values for the apparent yield of  $H_2$  were not affected by reactions in the gas-vapor phase of an ampule either during or subsequent to the irradiation of the ampule and, accordingly, that the apparent yield of  $H_2$  in an ampule experiment was equal to the actual yield.

The results of the fewer experiments conducted at temperatures in the ranges 30 to 45°C and 100 to 143°C provided evidence that at these temperatures also there were no significant effects on the yields of  $H_2$  resulting from differences between the relative volumes of solution and gas-vapor phases in an ampule irradiation. However, the values for  $G(H_2)_w$  with experiments in these temperature ranges depended upon which

of the two ampule-loading procedures was used. The possibility that  $\text{Cl}_2$  formation accounted for this dependence is discussed in Sect. 10.6.

### 10.3 Brief Review and Analysis of Literature on the Radiation-Induced Formation of HCl from $\text{Cl}_2$ and $\text{H}_2$ in a Gas Phase

Radiation-induced reactions to form HCl mixtures from  $\text{Cl}_2$  and  $\text{H}_2$  occur by chain reactions with chain lengths that depend upon the purity of the gases. Effective values of  $M(\text{HCl})/N$  ranging from about 900 to  $5.1 \times 10^5$  were reported by Lind and coworkers,<sup>11,12</sup> who ascribed the variations to differences in the purities of the test mixtures. It is known that the addition of  $\text{O}_2$  to a mixture of  $\text{H}_2$  and  $\text{Cl}_2$  reduces the chain length. Chapman and MacMahon<sup>13</sup> cite Bunsen and Roscoe<sup>14</sup> for evidence that the addition of 5 parts of  $\text{O}_2$  to 1000 parts of stoichiometric mixture of  $\text{H}_2$  and  $\text{Cl}_2$  reduces the chain length of the photo-induced reactions by a factor of about 10. Others have reported that addition of  $\text{N}_2$  to a stoichiometric mixture of  $\text{H}_2$  and  $\text{Cl}_2$  increases the radiolytic yield of HCl.<sup>15</sup> We assumed that this  $\text{N}_2$  effect resulted from charge transfer between the  $\text{N}_2$  and the  $\text{Cl}_2$  and/or  $\text{H}_2$ . For reference and comparison purposes, it can be noted that a value of 1000 for  $M(\text{HCl})_v/N$  corresponds to  $G(\text{HCl})_v = 2800$ , assuming that  $W$  (energy expended to form an ion pair) equals 35 eV in the given gas-vapor mixture and that all ion pairs cause formation of 1000 HCl regardless of the gas species that is ionized [analogous assumptions were made in obtaining values for  $G(\text{H}_2\text{O})_v$  in reactions between  $\text{H}_2$  and  $\text{O}_2$  in the gas phase, see footnote d, Table 3].

### 10.4 Conceivable Effects on $\delta$ of Radiation-Induced Gas-Phase Formation of HCl

The information discussed in the previous section indicated that reactions between  $\text{H}_2$  and  $\text{Cl}_2$  in the gas phase could have a substantial effect on the apparent yield of  $\text{H}_2$  in an ampule if  $\text{Cl}_2$  is in fact a product of radiolysis of brine solution and if some of the  $\text{Cl}_2$  enters a gas phase. The amount of  $\text{H}_2$  converted to HCl in a given experiment would depend upon several different factors, including the following.

- a. The composition of the gas-vapor mixture over the solution within the ampule, particularly the amount of air in the mixture.
- b. The composition of the gas bubbles that are formed within the solution as radiolysis proceeds (and by which radiolytic gases escape from the solution) and the length of time that a given portion of the gas bubble remains within the solution. It is likely that the value for  $G(\text{HCl})_v$  within the bubble would differ from, and probably exceed, that in the gas-vapor mixture above the solution because of difference between the compositions of gases within the two regions. The bubbles would probably contain a smaller fraction of air, for example, than the fraction contained in the gas-vapor mixture above the solution.
- c. The temperature of the ampule during irradiation through effects on other factors, including (1) solubility of  $\text{Cl}_2$  in the solution, (2) residence time of gas bubbles within the solution, and (3) reactions of dissolved  $\text{Cl}_2$  to form other chlorine species such as  $\text{ClO}_3^-$ .

#### 10.5 Possibilities That Radiolytic $\text{Cl}_2$ Accounted for Observed Deficits of $\text{O}_2$

Each of the experiments with brine solutions except No. 62 showed a deficit or radiolytic  $\text{O}_2$  in the gas phase (i.e., the value for the quantity  $2G(\text{O}_2)_w / G(\text{H}_2)_w$  in each of these experiments was  $<1$ ; see Table 11). The result of analyses for  $\text{H}_2\text{O}_2$ ,  $\text{ClO}_3^-$ , and  $\text{Cl}_2$  in the irradiated solutions indicated that the amounts of these species were much too small to explain the deficits. In the case of  $\text{Cl}_2$ , it is possible that some of this species, if present, could have escaped detection by the analytical methods and procedures which were employed. Thus,  $\text{Cl}_2$  would have been retained within the ampule at liquid nitrogen temperatures when the more volatile gases ( $\text{He}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{N}_2$ ) were extracted for analyses with the mass spectrometer.\* Subsequently, but prior to the analyses of the irradiated solutions, the gaseous  $\text{Cl}_2$  might have escaped

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\*Probably more than 50% of the chlorine would have been dissolved in the solution as  $\text{HClO}$ ,  $\text{Cl}_3^-$ , and  $\text{Cl}_2$ .<sup>16</sup>



from the stoppered ampule (to react with the cork stopper or to move into the ampule surroundings). However, on the basis of the evidence presented in Sects. 10.2 and 10.6 that there were no effects on  $G(\text{H}_2)_w$  of reactions in the gas-vapor space over the solution in ampules irradiated in the temperature range 73 to 85°C, we believe that  $\text{Cl}_2$  did not accumulate in any ampule in amounts sufficient to account for the deficit of  $\text{O}_2$  observed in the ampule.

#### 10.6 Possibilities That Radiolytic $\text{Cl}_2$ Accounted for Observed Effects of Loading Procedure on $G(\text{H}_2)_w$

Effects of loading procedure on  $G(\text{H}_2)_w$  were observed with those ampule experiments that were irradiated in the temperature ranges of 30 to 45°C and 100 to 143°C (Table 11). Those experiments in which loading procedure A\* was employed gave values for  $G(\text{H}_2)_w$  that averaged 33% and 41% greater than the average of those in which loading procedure B\* was employed and which were irradiated within the same range of temperatures, 100 to 143°C and 30 to 45°C, respectively. Loading procedure A left more air (5 to 8%) in an ampule than did loading procedure B (<1% air),\*\* and it can be tentatively postulated that the values  $G(\text{H}_2)_w$  were affected by formation of  $\text{HCl}$  from radiolytic  $\text{H}_2$  and  $\text{Cl}_2$  in the gas-vapor phase within an ampule and that a lowered value for  $G(\text{HCl})_v$  with a resulting increase of the net yield of  $\text{H}_2$  occurred in the presence of the larger amounts of air.

However, as stated in Sect. 10.2, no effects of loading procedure on  $G(\text{H}_2)_w$  (with the possible exception of experiment No. 6) were observed in experiments with ampules that were irradiated at temperatures in the range 73 to 85°C. Accordingly, the validity of the above postulate is questionable. It appears that the mere presence of a relatively large fraction of air within the gas-vapor mixture over the test solution did not explain all effects of loading procedure on the apparent yield of  $\text{H}_2$ . Some other agent or agents within an ampule must have been acting

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\*Loading procedures A and B are described in Table 2, footnote e.

\*\*Except experiment No. 62 (Table 6).

to inhibit (at 73 to 85°C) or to accentuate (at 30 to 45°C and 106 to 143°C) the apparent effects of the loading procedure and/or of the relatively large amounts of air. These other agents have not been identified.

#### 10.7 Possibilities That Apparent Yields of $H_2$ Were Reduced by Formation of HCl from $Cl_2$ and $H_2$ within Gas Bubbles in the Solution during Irradiation

These possibilities were not completely eliminated by the results of evaluations of the available experimental and theoretical information.\*

From a practical standpoint, we are interested in the yield of  $H_2$  into the gas-vapor space above an irradiated solution, and it is immaterial whether or not a significant amount of reaction between  $H_2$  and  $Cl_2$  (or other species) takes place within gas bubbles if the net effect on  $G(H_2)_w$  does not change with solution composition or other exposure variable. The results with B-loaded ampules showed that negligible effects on  $G(H_2)_w$  resulted from substantial changes on each of several different exposure variables. The effects on  $G(H_2)_w$  of changes in loading procedure along with maintaining the temperature within certain ranges during exposure to gamma radiations are conceivably related to gas-phase reactions within bubbles, and more experimental work is needed to verify or discount this conception.

#### 10.8 Yields of $H_2$ from Gamma-Irradiation of Highly Concentrated $MgCl_2$ Solution at 150 to 160°C and 169 to 182°C

The loading procedure employed with these experiments most closely simulated procedure B (see Sect. 2.6 and Table 8).

As shown in Table 11, the average value for  $G(H_2)$  equaled 0.79 for the two experiments at 169 to 182°C. This value is appreciably greater than that found with B-loaded experiments with solutions of lower concentrations and at temperatures <143°C. Also, as discussed in Sect. 7,

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\*The near agreement among the values for  $G(H_2)_w$  for all of the B-loaded ampule experiments suggests that such reactions within bubbles had negligible effects on  $G(H_2)_w$  in these experiments (see Sect. 10.4).

the possibilities were not excluded that the formation of  $H_2O$  from  $H_2$  and  $O_2$  in the gas-vapor phase was sufficient to effect significant reductions in the apparent values of  $G(H_2)$  in these high-temperature experiments. If we assume that this lowering was equal to the maximum amount predicted from the indirect experimental information of Lind et al.,<sup>5-8</sup> the actual average value for  $G(H_2)$  was 1.05.

Similarly, the actual average value for the two experiments at 150 to 160°C would be 0.62 rather than the unadjusted value of 0.50. However, this unadjusted value is very near the average values for  $G(H_2)_w$  found with B-loaded experiments with solutions of lower concentrations and lower temperatures. It is possible that there were no significant effects of temperature or of  $MgCl_2$  concentrations in B-loaded experiments, up to and including the temperatures and concentrations employed in the 150 to 160°C experiments.

No explanation is known for the occurrence of the relatively high  $H_2$  yield in the 169 to 182°C experiments. It is likely, however, that the increased hydrolysis and  $HCl$  formation at the high temperatures and concentrations contributed to the higher yields.

No information was obtained on the possibilities that  $Cl_2$  formation and reaction with  $H_2$  in the gas phase affected the values for  $G(H_2)_w$  in these experiments.

#### 10.9 Possibilities That Dissolution of $O_2$ within Test Solution Accounted for Deficits of $O_2$

As shown in Appendix E, it is very unlikely that a significant fraction of any of several gaseous species ( $H_2$ ,  $O_2$ ,  $N_2$ , or  $He$ ) within an ampule were dissolved in the liquid phase at equilibrium.

It is likely that equilibrium prevailed by the time an ampule was immersed in liquid nitrogen prior to expanding the gases into the gas-handling system attached to the mass spectrometer.

## 11. CONCLUSIONS

### 11.1 Values for $G(\text{H}_2)$ and $G(\text{O}_2)$ in NaCl-Saturated $\text{MgCl}_2$ Solutions in the Temperature Range 30 to 143°C

#### 11.1.1 Deaerated solutions

We concluded that the yield of  $\text{H}_2$  from a gamma-irradiated brine solution into a simultaneously irradiated, deaerated atmosphere above the solutions\* is between 0.48 and 0.49 over most of this range of temperatures. However, the yield is probably somewhat lower at the lower end of this temperature range;  $G(\text{H}_2)$  averages 0.44 at 30 to 45°C. Changes in the relative amounts of  $\text{MgCl}_2$  and NaCl in the NaCl-saturated solutions have negligible effects on the yield.

The yield of  $\text{O}_2$  into the deaerated atmosphere in the same systems averages 0.13, independently of temperature and brine composition.

The relative values for  $G(\text{O}_2)$  and  $G(\text{H}_2)$  in these experiments are shown by the following ratio:

$$2G(\text{O}_2)/G(\text{H}_2) \approx 0.5 . \quad (14)$$

The value of 0.5 for this ratio shows that only about half of the radiolytic oxidant that was formed along with the  $\text{H}_2$  was present as  $\text{O}_2$ . We did not succeed in identifying the species composing the remainder of the oxidant.

#### 11.1.2 Aerated solutions

We concluded that the yield of  $\text{H}_2$  from a gamma-irradiated brine solution into a simultaneously irradiated, contacting atmosphere containing 5 to 8% air\*\* may be greater than the yield in deaerated systems by amounts ranging from about 0 to 40% depending upon temperature, 0%

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\*He at 1 atm and at room temperature with pressure increasing with temperature within the sealed test systems, and  $\text{H}_2\text{O}$  vapor at saturation pressure for the given brine solution.

\*\*Five to 8% air in He at 1 atm total pressure at room temperature, with pressure increasing with temperature in sealed test systems, and  $\text{H}_2\text{O}$  vapor at saturation pressure for the given brine solution.

for temperatures of 73 to 85°C and 30 and 40% for temperatures in the ranges 100 to 143°C and 30 to 45°C, respectively.

The apparent yield of  $O_2$  in these aerated systems was zero.

We did not succeed in establishing the mechanisms whereby the air affected the yields of  $H_2$  and  $O_2$ . We speculated that  $O_2$  within gas bubbles rising through the irradiated solution inhibited back reactions of  $H_2$  and  $Cl_2$  that would otherwise take place. With respect to the zero  $O_2$  yield, we speculated that results of the mass spectrometer analyses for  $O_2$  were in error by amounts and in the direction that account for the apparent absence of radiolytic  $O_2$ .

### 11.1.3 Comparisons with reported and/or predicted $G$ values

The values for  $G(H_2)$  in deaerated systems found in this work are in approximate agreement with the value of 0.44 for the gamma-irradiation yield of  $H_2$  in pure  $H_2O$  at room temperature.<sup>3</sup> They are also in agreement with the values predicted by extrapolation of the findings reported by others<sup>3</sup> that the value for  $G(H_2)^*$  in 2 M NaCl solutions at room temperature is not appreciably different from that in pure  $H_2O$ . They are in poorer agreement with  $G(H_2) = 0.42$  stated by Spitsyn et al.<sup>1</sup> for NaCl-saturated solutions in the range 0 to 85°C. They completely discount the higher values for  $G(H_2)$  in brine ( $\sim 2$ ) inferred from results with KCl solutions reported by previous Russian workers.<sup>2,3,17</sup>

The value for  $G(O_2)$  in our deaerated solutions is  $\sim 65\%$  greater than the value [ $G(O_2) = 0.08$ ] stated by Spitsyn et al.<sup>1</sup> for NaCl solutions at room temperature.

Our indication of effects of 5 to 8% air on the values for  $G(H_2)$  in an experiment apparently does not agree with the stated findings of Spitsyn et al.,<sup>1</sup> that the value for  $G(H_2)$  in salt solutions is independent of  $O_2$ .

The absence of significant effects of temperature on the yield of  $H_2$  in our deaerated experiments and as stated by Spitsyn et al.<sup>1</sup> is in agreement with the predictions for pure  $H_2O$ .<sup>2,3</sup>

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\* $G(H_2)$  represents the initial yield of  $H_2$  into homogenous distribution within the irradiated solution.

### 11.2 Values for $G(H_2)$ in 10 m to 12 m $MgCl_2$ Solutions, NaCl-Saturated and Deaerated, at Temperatures of 150-182°C

We concluded that the values for  $G(H_2)$  in these solutions were greater than those for solutions of lower  $MgCl_2$  concentrations at lower temperatures by factors which ranged from  $\sim 1.0$ -1.25 at 150-160°C to 1.6-2.0 at 169-182°C. Presumably, the increased hydrolysis of  $MgCl_2$  at higher temperatures and concentrations was responsible for some or all of the increases in  $G(H_2)$ .

### 11.3 Radiolysis of $MgCl_2 \cdot 6H_2O$ Crystals

We found that radiolytic decomposition of the water of hydration in this hydrate takes place, but that the effective values for  $G(H_2)$  are much less than those in a liquefied solution with the same ratio of  $MgCl_2$  to  $H_2O$ .

Also, we found that most of the  $H_2$  is not released from the crystals until the irradiated material is heated above the liquefaction temperature.

### 11.4 Recommended Additional Work

Some additional work would help in the identification of the several oxidized species that are apparently formed in the radiolysis of brine solutions and also in the further clarification of the mechanisms of radiolysis in the brines:

- a. recalibrate the mass spectrometer for  $O_2$  analysis at the low levels of  $O_2$  that are used in our ampule irradiations;
- b. conduct ampule irradiations of NaCl-saturated  $MgCl_2$  solutions followed within a period of  $\sim 1$  d by analyses of the irradiated solutions for  $H_2O_2$ ,  $Cl_2$ ,  $ClO_3^-$ , and  $ClO_4^-$ ;
- c. conduct ampule irradiations of NaCl- $MgCl_2$  brine solutions with  $O_2$ -He and  $N_2$ -He atmospheres followed by mass spectrometer analyses of gases, especially  $H_2$ , within the ampules; and
- d. conduct other irradiation experiments as suggested by the results of a, b, and c.

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### 13. APPENDIXES



# Appendix A. Results of Solution and/or Gas Analyses of Unirradiated Controls

Experiment No. <sup>a</sup> and solution	Volume (mL)	Exposure conditions		Results of analyses of gases ( $\mu\text{mol}$ )				Results of analyses of solutions ( $\mu\text{g/mL}$ )		
		Temperature (°C)	Time (min)	Total	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	ClO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> O <sub>2</sub>	Cl <sub>2</sub>
T-1 <sup>b</sup>		Room							0.105	
50	2.23	Room		125	0	0.15	0.32	0.70		
51	2.21	Room		132	0	0.17	0.37		<0.04	
63	1.72	79-92	60	144	0	0.03	0.10	0.50		
64	1.71	70-90	60	141	0	0.02	0.04			<0.05
65	1.71	119-140	60	136	0	0.01	0.03	0.64		
66	1.72	119-140	60	138	0	0.01	0.03			<0.05
T-3 <sup>c</sup>		Room						0.51	0.18	
67	1.66	70-92	60	158	0	0.01	0.02	0.77		
68	1.70	70-92	60	155	0	0.01	0.03		0.20	
71 <sup>d</sup>		172-188	45	147	0	0.01	0.03			
72 <sup>e</sup>		172-188	45	162	0	0.01	0.03			
He reservoir <sup>f</sup>	0.002% H <sub>2</sub> , 99.39% He, 0.487% H <sub>2</sub> O, 0.083% N <sub>2</sub> +CO, 0.033% O <sub>2</sub> , 0.002% Ar, 0.002% CO <sub>2</sub>									
He reservoir <sup>g</sup>	0.001% H <sub>2</sub> , 99.559% He, 0.223% H <sub>2</sub> O, 0.168% N <sub>2</sub> +CO, 0.044% O <sub>2</sub> , 0.002% Ar, 0.003% CO <sub>2</sub>									

<sup>a</sup>Experiment Nos. 50-72 employed sealed ampules as with irradiation samples.

<sup>b</sup>Sample for analysis taken from stock; composition: 2.4 m MgCl<sub>2</sub>, 0.03 m in NaBr, and saturated NaCl.

<sup>c</sup>Sample for analysis taken from stock; composition: saturated in MgCl<sub>2</sub> (5.8 m) and NaCl and enough NaBr to make 0.08 m if all was in solution.

<sup>d</sup>This test solution was 11.0 m in MgCl<sub>2</sub> and saturated in NaCl. This solution was prepared by concentrating a sample of T-3 within an ampule by evaporation of H<sub>2</sub>O. The final ampule sample contained 1.12 g H<sub>2</sub>O.

<sup>e</sup>This test solution was 12.5 m in MgCl<sub>2</sub> and saturated in NaCl. This solution was prepared as described under footnote <sup>d</sup> above. The final ampule sample contained 0.93 g H<sub>2</sub>O.

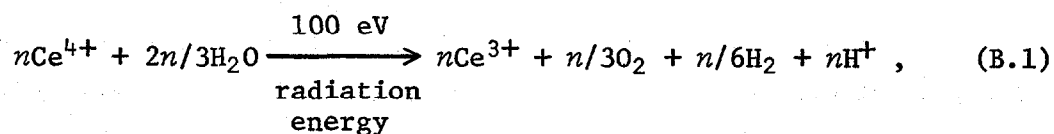
<sup>f</sup>Large sample taken during filling of He reservoir following experiment No. 43. This reservoir filling was used with ampules for experiment Nos. 44 through 62.

<sup>g</sup>Large sample taken during filling of He reservoir prior to experiment No. 63. This reservoir filling was used with ampules for that and subsequent experiments.

## Appendix B. Ceric Solution Dosimetry

The gamma dose rate in water at the ampule-irradiation site in the cobalt source was determined from the results of irradiations of a ceric sulfate dosimeter solution at the site.

The radiation-chemical reaction that is employed in ceric-solution dosimetry is the reduction of ceric ion to cerous ion:



where  $n$  represents the value of  $G(\text{Ce}^{3+})$  in the dosimeter solution.

The dose rate  $I_w$  ( $\text{eV}/\text{min} \cdot \text{g}_{\text{H}_2\text{O}}$ ), which prevails during irradiation of a ceric solution, is related to the change in molar concentration of ceric ( $\Delta \text{Ce}^{4+}$ ) and to other quantities:

$$I_w \cdot t (1 + E_s/E_w) = (\Delta \text{Ce}^{4+}/1000) (1/b) (6.023 \times 10^{23}) 100/G(\text{H}_2), \quad (\text{B.2})$$

where

$t$  = irradiation time, min;

$b$  = mass of  $\text{H}_2\text{O}$  per unit volume of ceric solution,  $\text{g}_w/\text{mL}_{\text{sol}}$ ;

$E_s/E_w$  = ratio of number of electrons associated with solutes to the number of those associated with the water containing the solutes.

The ceric solution used was  $\sim 500 \mu\text{molar}$  in  $\text{Ce}^{4+}$  and  $0.4 \text{ molar}$  in  $\text{H}_2\text{SO}_4$ . The density at  $25^\circ\text{C}$  was  $1.024 \text{ g/mL}$ .\* The value of  $b$  for this solution was then

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\*This solution was prepared by workers in Hochanadel's laboratory at ORNL in 1964, and was stored in his laboratory in the dark in a Pyrex bottle.<sup>1</sup> The density value and composition were reported by Hochanadel and/or by the bottle label. We confirmed the value for the concentration of  $\text{Ce}^{4+}$  in spectrophotometric measurements of the solution.

$$b = 1.024 - (0.4)(98/1000) = 0.985, \text{ g}_w/\text{mL}_{\text{sol}}, \quad (\text{B.3})$$

and the value of  $E_s/E_w$  was 0.0366.

Introducing these values for  $b$  and  $E_s/E_w$  into Eq. (B.2), along with the value of 2.50 for  $G(\text{Ce}^{3+})$ ,<sup>2,3</sup> simplifying, and rearranging yield

$$I_w = 2.35 \times 10^{22} \cdot \Delta \text{Ce}^{4+}/t. \quad (\text{B.4})$$

Analyses for  $\Delta \text{Ce}^{4+}$  were conducted spectrophotometrically using a Carey spectrophotometer and a quartz-window cell, 1 cm internal thickness and 2 cm diam, and measuring the absorption at 320 nm. The reported value for the extinction coefficient in the solution at 320 nm was 5580 (refs. 1, 2, and 4). Using this value,

$$\Delta \text{Ce}^{4+} = \Delta \text{OD}/5580, \quad (\text{B.5})$$

where OD = optical density =  $\log I_o/I_t$ . Now substituting from Eq. (B.5) in Eq. (B.4) and simplifying,

$$I_w = 4.21 \times 10^{18} \cdot \Delta \text{OD}/t, \text{ eV/g}_w \cdot \text{min}. \quad (\text{B.6})$$

Experimental measurements of  $\Delta \text{OD}/t$  along with the corresponding calculated values for  $I_w$  are reported in the text (Sect. 2.3). The values for  $I_w$  were calculated from the results of measurements using the relationship shown by Eq. (B.6).

#### References for Appendix B

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### Appendix C. Measurement of Amount of Gas within an Ampule

Figure C.1 indicates the several parts of the gas handling system, which was attached to the mass spectrometer (see Sect. 2.4). The symbols  $V_3$  and  $V_4$  refer to the volumes of the liquid-nitrogen-cooled portions of the U-trap and the ampule, respectively.

The value of  $V_1$  is known, and the volume of the remainder of the system was determined by introducing a gas into  $V_1$ ; measuring its pressure,  $P_i$ ; and temperature,  $T_r$ ; and then expanding the gas into the remainder of the system and measuring the resulting pressure,  $P_c$ .

The number of moles of gas,  $N_c$ , used in the calibration (assuming that the ideal gas law is adequate) is given by

$$N_c = P_i \cdot V_1 / R \cdot T_r . \quad (C.1)$$

( $P_i$  was usually  $\sim 8$  kPa.) We can also write

$$P_i \cdot V_1 / R \cdot T_r = N_c = (P_c / R) (V_1 / T_r + V_2 / T_r + V_3 / T_n + V_4 / T_n) , \quad (C.2)$$

and by rearranging and solving:

$$V_1 + V_2 + (V_3 + V_4) T_r / T_n = P_i \cdot V_1 / P_c . \quad (C.3)$$

Now when we want the number of moles of gas in the sample,  $N_s$ , the gas is confined within  $V_1 + V_2 + V_3 + V_4$ , and the pressure,  $P_s$ , is measured. Proceeding as above, we can write,

$$N_s = [P_s / R \cdot T_r'] [V_1 + V_2 + (V_3 + V_4) T_r' / T_n] , \quad (C.4)$$

where  $T_r'$  is room temperature at the time of the sample measurement.

Now substituting for  $V_1 + V_2$  in Eq. (C.4) from Eq. (C.3) and rearranging,

$$N_s = [P_s / R \cdot T_r'] [P_i \cdot V_1 / P_c + (V_3 + V_4) (T_r' / T_n - T_r / T_n)] , \quad (C.5)$$

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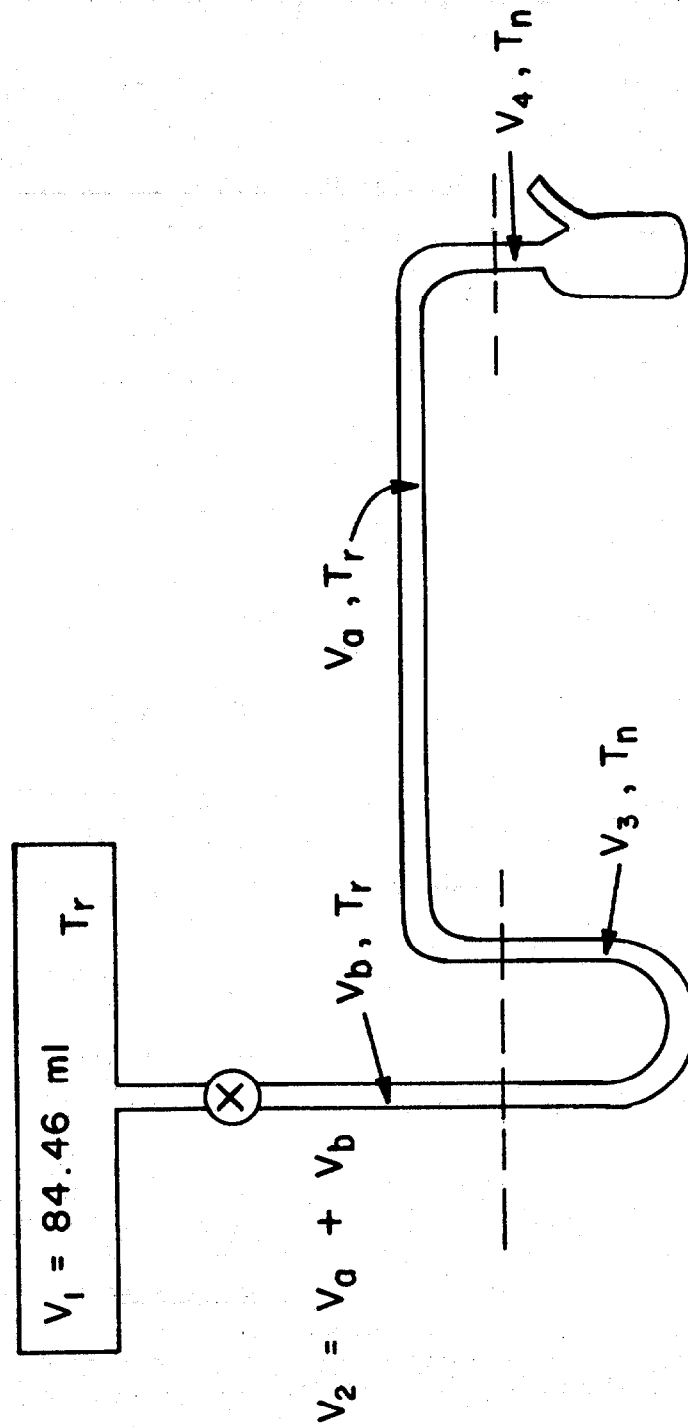


Fig. C.1. Parts of the gas handling system at the mass spectrometer.

when  $T_r' = T_r$ , Eq. (C.5) reduces to

$$N_s = (P_s / R \cdot T_r) (P_i \cdot V_1 / P_c) . \quad (C.6)$$

The measurements were conducted such that  $T_r' = T_r$  and such that  $V_3$  and  $V_4$  did not change between the calibration and the sample measurement. Then Eq. (C.6) was applicable and was used in the calculations of the amounts of gas in an ampule.

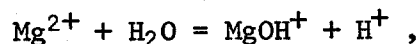


Appendix D. The Hydrolysis of  $\text{Mg}^{2+}$  in Concentrated Brines at 25°C

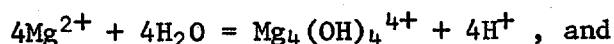
H. R. Bronstein and C. F. Baes, Jr.\*

A brief potentiometric study has been made of  $\text{MgCl}_2$ -NaCl mixtures to investigate the hydrolysis of  $\text{Mg}^{2+}$  ions in the concentrated brines that might occur in salt repositories. The method consists of titrating such solutions containing small known amounts of added HCl with concentrated solutions of NaOH, the purpose being to vary the pH and induce hydrolysis with as little change as possible in the composition of the solution.

The previous work on the hydrolysis of  $\text{Mg}^{2+}$  ion was reviewed by Baes and Mesmer<sup>1</sup> and summarized in terms of the following two reactions and their corresponding equilibrium quotients:



$$\log Q_{11} = -11.44 - 1.022\sqrt{I}/(1 + \sqrt{I}) - 0.34 \, m_{\text{Cl}},$$



$$\log Q_{44} = -39.71 + 2.044\sqrt{I}/(1 + \sqrt{I}) - 0.45 \, m_{\text{Cl}}.$$

Thus only two hydrolysis products were necessary to explain the data,  $\text{MgOH}^+$  and a tetramer,  $\text{Mg}_4(\text{OH})_4^{4+}$ . The first term in each expression for the formation quotient corresponds to the equilibrium constant at zero ionic strength ( $I$ ); the second term is the Debye-Huckel correction for the effect of ionic strength, and the last term represents the effect of the anion molarity of the solution. These expressions are based on measurements that extend to chloride concentrations of 3  $m$  and ionic strengths of 4.5  $m$ .<sup>2</sup> The primary purpose of the present study was to examine the hydrolysis of  $\text{Mg}^{2+}$  at the higher chloride concentrations and ionic strength that occur in NaCl-saturated brines.

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\*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

The solutions were prepared by weight from Fisher Scientific  $\text{MgCl}_2$  of 99.9% purity and Harshaw optical-grade  $\text{NaCl}$ . The titration cell contained a combination (glass-Ag,  $\text{AgCl}$ ) electrode in which the liquid forming the salt bridge was of nearly the same composition as the solution being titrated. Titrant ( $\text{NaOH}$ ) was delivered from a micrometer-driven syringe through a teflon capillary delivery tube. The cell, thermostated at  $25^\circ\text{C}$ , was purged continuously with a slow stream of nitrogen. The potential of the cell was measured with a precision of  $<0.1$  mV with a vibrating-reed electrometer as a detector and a Leeds & Northrup K-3 potentiometer. As is customary in such measurements, the standard for pH was the starting composition of the solution, which was precisely known. This permitted the conversion of the cell potentials to hydrogen ion concentrations throughout the titration, the only uncertainty being whatever small error was involved in estimating changes in the liquid junction potential. For details of this technique, see ref. 1, p. 10.

The results are summarized in Fig. D.1, where the average number of hydroxide ions bound per  $\text{Mg}^{2+}$  ion (called the ligand number) is plotted vs the pH. As can be seen, this ratio does not reach very high values before the titrations must be terminated because of the onset of hydrolytic precipitation. Each titration curve was fit by least squares, assuming the two hydrolysis products referred to above. The resulting formation quotients are plotted in Fig. D.2, showing fairly good agreement with the form of the expressions for  $\log Q$  shown above. The revised expression for each formation quotient is

$$\log Q_{11} = -11.44 - 1.022\sqrt{I}/(1 + \sqrt{I}) + 0.045 \, m_{\text{Cl}}$$

and

$$\log Q_{44} = -41.02 + 2.044\sqrt{I}/(1 + \sqrt{I}) - 0.154 \, m_{\text{Cl}} .$$

The smooth curves in Fig. D.1 were calculated using these expressions. They should permit considerably improved estimates of the hydrolysis of  $\text{Mg}^{2+}$  in  $\text{NaCl}$ -saturated brines at  $25^\circ\text{C}$ .

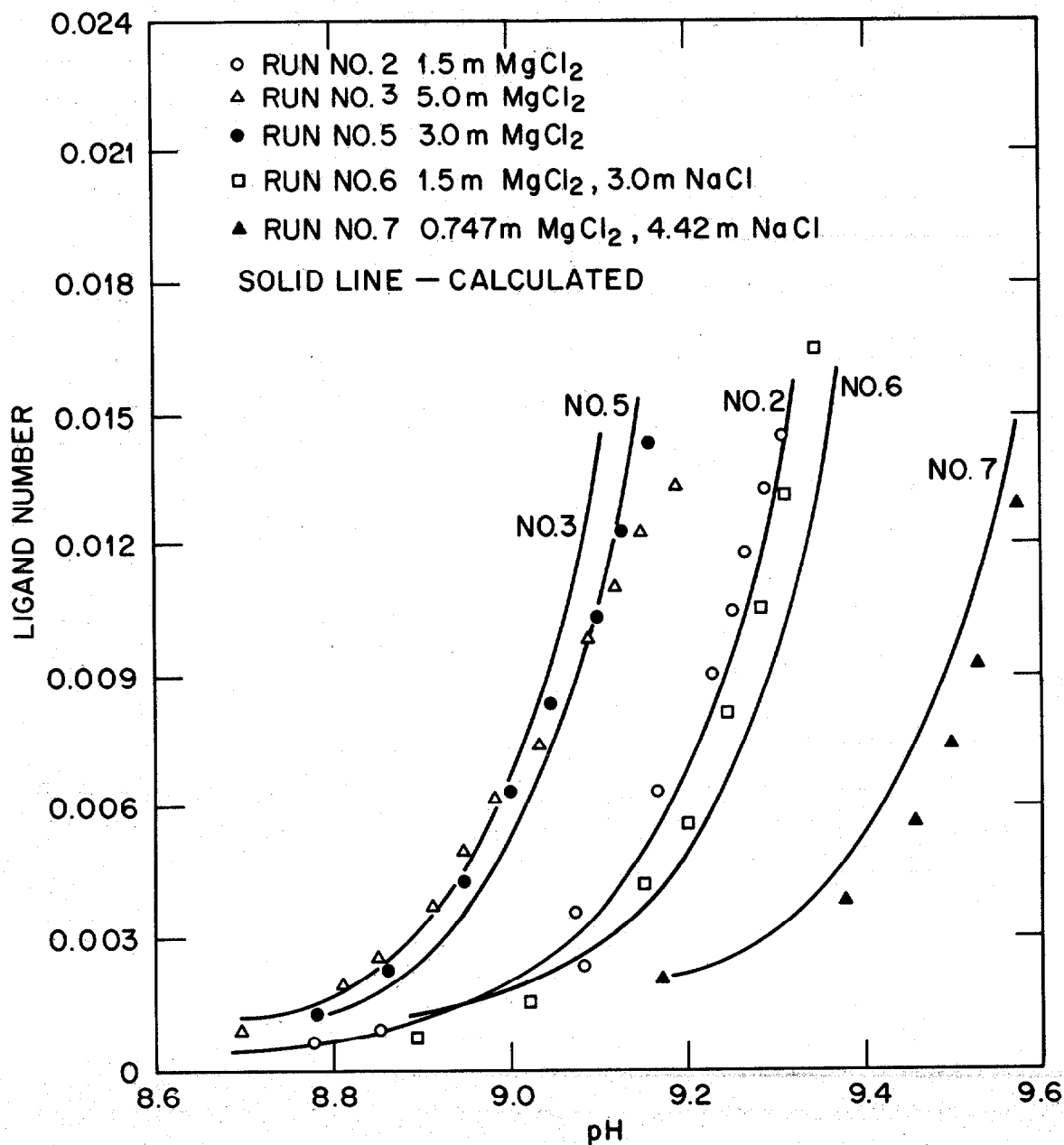


Fig. D.1. Results of potentiometric titration of  $\text{MgCl}_2$ - $\text{NaCl}$  solution. The ligand number is the average number of hydroxyl ions bound per  $\text{Mg}^{2+}$  ion in solution. The curves are calculated assuming the hydrolysis products are  $\text{MgOH}^+$  and  $\text{Mg}_4(\text{OH})_4^{4+}$ , with formation quotients given by the expressions in the text.

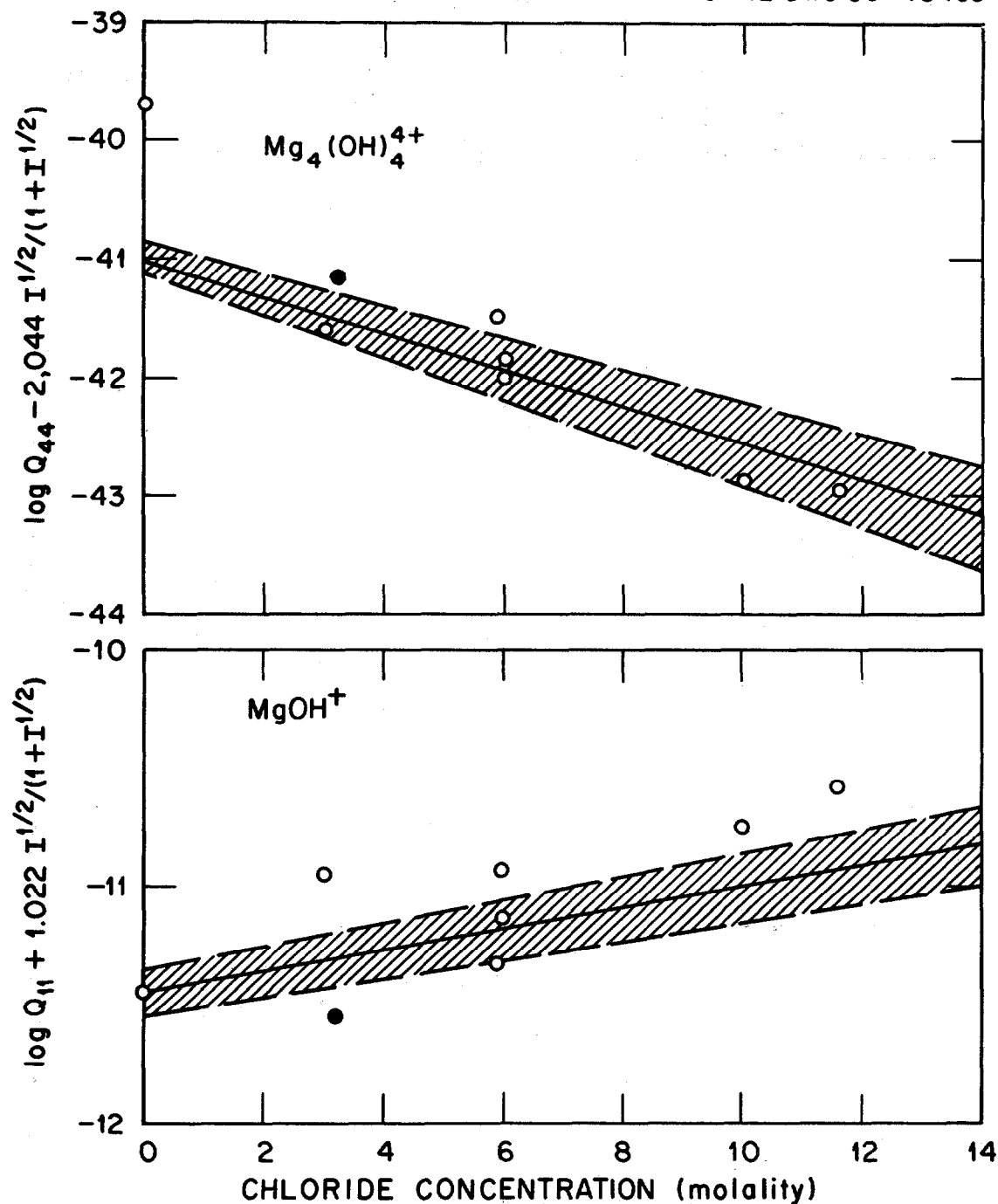


Fig. D.2. Variation of the formation quotients of  $\text{MgOH}^+$  and  $\text{Mg}_4(\text{OH})_4^{4+}$  with chloride molality. The open circles result from least-squares fits of the individual curves in Fig. D.1. The solid circles are based on previous data.<sup>2</sup> The lines result from fitting all the data with a formation of the form  $\text{Log } Q_{xy} = \text{Log } K_{xy} + a \sqrt{I}/(1 + \sqrt{I}) + b m_{\text{Cl}^-}$ . The bands indicate the uncertainty ( $3\sigma$ ) in the value of  $\text{Log } K_{xy}$  (the intercept) and  $b$  (the slope).

## References for Appendix D

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Appendix E. Possibilities That Dissolution of  $O_2$  within  
Test Solutions Accounted for Deficits of  $O_2$

A convenient relationship for use in the present considerations is,

$$N_1/N_g = W \cdot P_t / N_t \cdot \alpha'_s, \quad (E.1)$$

where

$N_1/N_g$  = ratio of moles of gas dissolved in solution to moles in  
gas phase, at equilibrium;

$W$  = mass of  $H_2O$  within liquid aqueous phase, kg;

$P_t$  = total pressure of gases within ampule at  $25^\circ C$  and  $\approx 1$  atm;

$N_t$  = total number of moles of gases within ampule at  $25^\circ C$  (values  
for this quantity and for  $W$  are listed in the data tables);

$\alpha'_s$  = solubility coefficient of gas in liquid aqueous phase,  
atm  $\cdot$  kg  $H_2O$ /mole gas.

Eq. (E.1) was derived using the general procedures and assumptions  
described in Appendix B of ref. 1.

Theory and experiment<sup>2-4</sup> show that the value for  $\alpha'_s$  in a salt  
solution is related to the value in pure  $H_2O$ ,  $\alpha'_w$ , by the equations

$$\gamma = \alpha'_s / \alpha'_w \quad (E.2)$$

and

$$(\log \gamma) / I = \theta, \quad (E.3)$$

where

$\gamma$  = activity coefficient for the given gas dissolved in salt  
solution,

$I$  = ionic strength of the salt in the solution,

$\theta$  = constant at a given temperature.

Some information from the literature on  $\theta$  values for  $O_2$ ,  $H_2$ ,  $N_2$ ,  
and He in NaCl solutions and for  $O_2$  in  $MgCl_2$  solutions at room temper-  
atures is summarized in Table E.1. The data were reported in several  
different units, as stated in the footnotes to the table. Where neces-  
sary, the reported data were converted to molal units to arrive at the

Table E.1. Reported values for the solubility of gases in salt solutions

Gas	Salt	Maximum concentration of salt ( <u>m</u> )	Temperature (°C)	$\theta$ (molal units)	Reference	Year	Notes
O <sub>2</sub>	NaCl	6.6	25	0.112	5	1974	<i>a</i>
O <sub>2</sub>	NaCl	2.1	25	0.132	2	1927	<i>b</i>
O <sub>2</sub>	NaCl	1.5	25	0.129	6	1950	<i>c</i>
O <sub>2</sub>	NaCl	4.0	25	0.118	7	1916	<i>c</i>
O <sub>2</sub>	MgCl <sub>2</sub>	1.9	20	0.083	6	1950	<i>c</i>
O <sub>2</sub>	MgCl <sub>2</sub>	5.0	25	0.064	7	1916	<i>c</i>
H <sub>2</sub>	NaCl	5.2	15	0.095	2	1927	<i>b</i>
N <sub>2</sub>	NaCl	2.3	25	0.205	2	1927	<i>b</i>
He	NaCl	5.8	25	0.055	8	1935	

<sup>a</sup>Data were reported in units of mole fraction.

<sup>b</sup>Reported work comprised a review and analysis of available literature information.

<sup>c</sup>Solubility data were reported as the Ostwald coefficient.

values for  $\theta$  that are listed in the table. We did not find any reported data for solubilities of  $H_2$ ,  $N_2$ , or He in  $MgCl_2$  solutions. However, theoretical considerations reported by others<sup>2</sup> indicate that the value of  $\theta$  for a given gas in  $MgCl_2$  solutions should be about the same as that in NaCl solutions. We found no reported information on the solubilities of gases in solutions containing both  $MgCl_2$  and NaCl.

Using the minimum tabulated value for  $\theta$  for  $O_2$  in  $MgCl_2$  solutions, the calculated value for  $\gamma$  in a saturated solution (5.83 m  $MgCl_2$ ) is 13. Since the value for  $\alpha'_w$  for  $O_2$  at 25°C is 790,<sup>9</sup> the corresponding value for  $\alpha'_s$  is  $1.0 \times 10^4$ . Using this value for  $\alpha'_s$  in Eq. (E.1), along with values for  $W$  and  $N_t$  for representative experiments, Nos. 14 and 24 (Table 2), we find values for  $N_1/N_g$  of  $3.9 \times 10^{-4}$  and  $2.4 \times 10^{-3}$ , respectively, indicating negligible amounts of dissolved  $O_2$  in the ampules at equilibrium.

Similarly, if we assume that the relationship

$$\log \gamma = (\theta \cdot I)_{NaCl} + (\theta \cdot I)_{MgCl_2} \quad (E.4)$$

prevails in a solution containing both NaCl and  $MgCl_2$ , we find  $\gamma = 5.0$  for  $O_2$  in a solution 2.4 m in  $MgCl_2$  and 2.1 m in NaCl at 25°C (using minimum tabulated  $\theta$  values). Then with  $\gamma = 5.0$ , the values for  $N_1/N_g$  for  $O_2$  in the experimental systems mentioned above are  $9.8 \times 10^{-4}$  and  $7.8 \times 10^{-3}$ , again indicating negligible fractions of dissolved  $O_2$  at equilibrium.

Using  $\theta$  values from Table E.1, the assumptions indicated by Eq. (E.4), and the assumption mentioned above regarding the approximate equality of  $\theta$  values in NaCl and  $MgCl_2$  solutions, analogous calculations for  $N_2$ ,  $H_2$  and He showed similar small values for the fractions of these gases that were dissolved in the solution within an ampule.

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